

REPORT DOCUMENTATION PAGE

*Form Approved
OMB No. 0704-0188*

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	1996		
4. TITLE AND SUBTITLE A Regional Analysis of Non-Methane Hydrocarbons And Meteorology of The Rural Southeast United States			5. FUNDING NUMBERS
6. AUTHOR(S) Lisa Marie Hagerman			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AFIT Student Attending: University of North Carolina			8. PERFORMING ORGANIZATION REPORT NUMBER 96-041
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) DEPARTMENT OF THE AIR FORCE AFIT/CI 2950 P STREET, BLDG 125 WRIGHT-PATTERSON AFB OH 45433-7765			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release IAW 190-1 Distribution Unlimited BRIAN D. GAUTHIER, MSgt, USAF Chief Administration			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words)			
14. SUBJECT TERMS			15. NUMBER OF PAGES 93
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to **stay within the lines** to meet **optical scanning requirements**.

Block 1. Agency Use Only (Leave blank).

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year.

Block 3. Type of Report and Dates Covered.

State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract	PR - Project
G - Grant	TA - Task
PE - Program Element	WU - Work Unit
	Accession No.

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number. (If known)

Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of...; To be published in.... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement.

Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR).

DOD - See DoDD 5230.24, "Distribution Statements on Technical Documents."

DOE - See authorities.

NASA - See Handbook NHB 2200.2.

NTIS - Leave blank.

Block 12b. Distribution Code.

DOD - Leave blank.

DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports.

NASA - Leave blank.

NTIS - Leave blank.

Block 13. Abstract. Include a brief (*Maximum 200 words*) factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code (*NTIS only*).

Blocks 17. - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

ABSTRACT

HAGERMAN, LISA MARIE. Regional Analysis of Non-methane Hydrocarbons and Meteorology of the Rural Southeast United States. (Under the direction of Viney P. Aneja).

Measurements of non-methane hydrocarbons, as well as ozone, meteorological and trace gas data, were made at four rural sites located within the southeastern United States as a part of the Southern Oxidants Study. Fifty-six C₂-C₁₀ hydrocarbons were collected from 1200-1300 local time, once every six days from September 1992 through October 1993. The measurements were made in an effort to enhance the understanding of the behavior and trends of ozone and other photochemical oxidants in this region. The light molecular weight alkanes (ethane, propane, n-butane, iso-butane), ethene and acetylene display a seasonal variation with a winter maximum and summer minimum. Isoprene was virtually non-existent during the winter at all sites, and averaged from 9.8 ppbC (Yorkville, GA) to 21.15 ppbC (Centreville, AL) during the summer. The terpene concentration was greatest in the summer with averages ranging between 3.19 ppbC (Centreville, AL) to 6.38 ppbC (Oak Grove, MS), but was also emitted during the winter months, with a range of 1.25 to 1.9 ppbC for all sites. Propylene-equivalent concentrations were calculated to account for differences in reaction rates between the hydroxyl radical and individual hydrocarbons, and to thereby estimate their relative contribution to ozone, especially in regards to the highly reactive biogenic compounds such as isoprene. It was calculated that biogenics represent at least 65% of the total non-methane hydrocarbon sum at these four sites during the summer season when considering propylene-equivalent concentrations. An ozone episode which occurred from July 20 to July 24 1993 was used as an example to show ozone profiles at each of the sites, and to show the effect of synoptic meteorology on high ozone by examining NOAA daily weather maps and climatic data. Relationships between meteorological variables such as temperature, relative humidity, solar radiation, and trace gases such as ozone, SO₂, CO and NO_y were also examined. A multiple regression on ozone at the Yorkville site found

temperature, relative humidity and NO_x to be statistically significant, with an R-square of 0.66.

A multiple regression using meteorological and trace gas data as input parameters and ARMA (autoregressive moving average) time series errors was applied to model daily average ozone, using data collected from June 1 through August 31 1992 at Yorkville, a rural site located in Pauldin County, Georgia. This statistical model was then applied to the same site for the 1993 summer, and the predicted and observed ozone values were compared using statistical tests. It was found that, while a good regression model was fitted for the 1992 ozone data, the same model tended to underpredict observed ozone concentrations for the 1993 summer. Ozone was found to be statistically higher in 1993 than in 1992 (with a 1993 average of 63.5 ± 16.6 ppb and a 1992 average of 50.25 ± 14.8 ppb), and this appears to be explained by the synoptic meteorology characterizing the 1993 summer, which was conducive to high ozone formation. A multiple regression model with time series errors was not found to be adequate in predicting ozone concentrations, because other factors affecting ozone levels, such as synoptic meteorology and atmospheric chemistry, also need to be considered.

**A REGIONAL ANALYSIS OF
NON-METHANE HYDROCARBONS AND METEOROLOGY
OF THE RURAL SOUTHEAST UNITED STATES**

by

LISA MARIE HAGERMAN

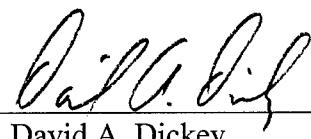
A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master of Science

DEPARTMENT OF MARINE, EARTH AND ATMOSPHERIC SCIENCES

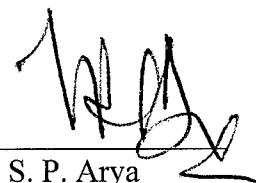
Raleigh

1996

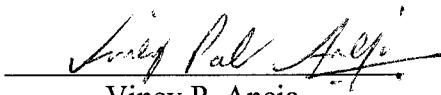
APPROVED BY:



David A. Dickey



S. P. Arya


Viney P. Aneja
Chair of Advisory Committee

BIOGRAPHY

Lisa Marie Hagerman was born in Taipei, Taiwan on May 10, 1972, as the first of two children to Cline R. and Judy ~~Hagerman~~ ^{Hageman}. After her father's retirement from the U.S. Navy, her family moved to Florida March 2, 1974, then two months later settled down in Colorado Springs, Colorado on May 9, 1974. In addition to doing well in academics, Lisa was heavily involved in music as a violinist for her Coronado High School orchestra, and as a member of the Colorado Springs Youth Symphony. She entered a completely new chapter in her life when she became Basic Cadet Hagerman on the sunny morning of June 29, 1990, her first day at the U.S. Air Force Academy in Colorado Springs. After four years of stress and much introspection, she finally graduated with a BS in physics on June 1, 1994, and was commissioned as a Second Lieutenant in the United States Air Force. Two months later she began her graduate studies at North Carolina State University. ~~After graduation, Lisa~~ ^{Upon graduation,} she married Steve Laskowski, an AF Academy 1993 graduate, in Manitou Springs, Colorado. After the 1996 summer, she will live with her husband in Papillion, Nebraska, and begin her next assignment at Offutt AFB, where she will serve as a weather officer with the 55th operations support squadron.

ACKNOWLEDGMENTS

I would like to acknowledge the United States Air Force for allowing me to return to school for my masters degree and for providing the financial assistance. I appreciate the guidance, support, and encouragement from my advisor Dr. Viney P. Aneja during the preparation of this thesis. I also thank the statistics representative of my committee, Dr. Dave Dickey, for his assistance in answering many of my questions on time series, and questions concerning the statistical programming involved in SAS®. I also appreciate the guidance of the third member of my committee, Dr. S.P. Arya.

This research has been partly funded by the North Carolina Department of Environment, Health and Natural Resources (NCDEHNR) under contract J-4004, and by the Southern Oxidants Study subcontract number G-35-693-54. I wish to thank George Murray and Thomas Manuszak of NCDEHNR for their assistance.

I'd like to thank Charlie Farmer at the University of Miami who helped me access the SOS-SCION hydrocarbon data; Shawn Roselle at the U.S. EPA for providing meteorological data; scientists at Environmental Science and Engineering, including Lynn Stanley, David Kirk, and Ben Hartsell, for also providing meteorological data as well as helping me with my questions. I also want to extend a special thanks to Bill Lonneman from the EPA, who took the time to read through my thesis drafts and helped get OH radical rate constants which I couldn't find in the literature.

I want to extend my appreciation to fellow members of Air Quality group, especially Mita Das, who has helped me immensely with her knowledge of hydrocarbons and organic chemistry.

Finally, I am grateful to my family: my parents Cline and Judy Hagerman, my brother Tom, and my husband Steve Laskowski, for their love and support.

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES.....	vi
INTRODUCTION.....	1
SECTION I: Regional Characterization of Non-Methane Hydrocarbons in the rural Southeast United States	5
Abstract.....	5
1. Introduction.....	6
2. Experiment	7
2.1. Site Description.....	7
2.2. Data Collection and Analysis.....	9
3. Results and Discussion.....	11
3.1. Measurements of C ₂ -C ₁₀ Speciated Hydrocarbons	11
3.2. Biogenic Hydrocarbons	27
3.3. Effect of Hydrocarbon Reactivity with Hydroxyl Radical.....	33
3.4. Relationship between Trace Gas and Meteorological Variables.....	39
Summary	55
References.....	57
SECTION II: Multiple Regression of Ozone Using Trace Gas and Meteorological Variables with Autoregressive Moving Average (ARMA) Time Series Errors	62
1. Introduction.....	62
2. Time Series Review: Autoregressive moving average (ARMA) processes	63
3. Results and Discussion.....	64
Summary	74
APPENDICES	75
Appendix A. Multiple Regression of 1992 Ozone Data with ARMA errors.....	76
Appendix B. Application of 1992 model for 1993 Ozone Data	80
Appendix C. Multiple Regression on 1993 ozone data with ARMA errors.....	83
Appendix D. Yorkville 1992 and 1993 Data	88
References.....	92

LIST OF TABLES

	Page
SECTION I	
Tables 1a-d. Seasonal averages of hydrocarbon compound concentrations in ppbC at:	
1a. Centreville, Alabama.....	12
1b. Oak Grove, Mississippi.....	14
1c. Yorkville, Georgia	16
1d. Candor, North Carolina	18
Table 2. Average hydrocarbon concentrations (ppbC) at various rural sites during the summer months.....	26
Table 3. Summer averages of biogenic hydrocarbons (ppbC).....	26
Table 4. Comparison of predicted isoprene values using regression equations from Jobson [1994], the regression of all sites, and the regression equation from only Centreville.....	31
Table 5. Correlation coefficients between biogenically emitted hydrocarbons and meteorological variables	32
Table 6. Rate constants k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reactions of OH radicals with hydrocarbons at $T=298^\circ\text{K}$	34
Table 7. Ten dominant hydrocarbons calculated in propylene-equivalent concentrations, listed in descending order	37
Table 8. Descriptive statistics of meteorological and trace gas data for all 4 sites ..	49
Table 9. Correlations between meteorological and trace gas variables.....	49

SECTION II

Table 1. Descriptive statistics of the Yorkville 1992 data.....	65
Table 2. Correlation coefficients between 1992 variables	65
Table 3. Descriptive statistics of the Yorkville 1993 data.....	70
Table 4. Correlation coefficients between 1993 variables	71

LIST OF FIGURES

	Page
SECTION I	
Figure 1. Map of sampling sites	8
Figure 2. Seasonal averages of select C ₂ -C ₄ hydrocarbons.....	21
Figure 3. Seasonal averages of hydrocarbon sums.....	23
Figure 4. Hydrocarbons with unusually high values.....	25
Figure 5a. Seasonal average of isoprene	28
Figure 5b. Seasonal average of terpene sum (α -, β -pinene, limonene)	28
Figure 6. Isoprene concentration versus temperature for the months April through September (1992 and 1993).....	29
Figure 7a. Hydrocarbon sums calculated in propylene-equivalent concentrations for the summer season.....	36
Figure 7b. Hydrocarbon sums calculated in propylene-equivalent concentrations for the winter season	36
Figs 8a-d. National Weather Service maps	
8a. Sfc map and 500 mb height contours at 7am EST, Monday July 19, '93..	40
8b. 500 mb height contours at 7am EST, Tuesday July 20, 1993	41
8c. 500 mb height contours at 7am EST, Wednesday July 21, 1993	41
8d. 500 mb height contours at 7am EST, Thursday July 22, 1993	42
8e. 500 mb height contours at 7am EST, Friday July 23, 1993	42
8f. 500 mb height contours at 7am EST, Saturday July 24, 1993	43
8g. Sfc map and 500 mb height contours at 7am EST, Sunday July 25, '93 ...	44
Figure 9. Diurnal profiles of ozone during an episode which occurred on July 20-25 1993	46
Figure 10. Seasonal averages of trace gases measured during the hydrocarbon sampling period	48
Figure 11. NO _y -NO versus ozone	50
Figure 12. Multiple regression of ozone at Yorkville, summer 1993	53

LIST OF FIGURES (CONTINUED)

	Page
SECTION II	
Figure 1. Multiple regression of Yorkville 1992 ozone data with ARMA errors	67
Figure 2. 1992 statistical model using 1993 data overlaid with observed ozone	68
Figure 3a. Time series of ozone residuals (observed - predicted).....	69
Figure 3b. Observed 1993 ozone versus residuals	69
Figure 4a. Yorkville 1993 multiple regression with ARMA errors.....	73
Figure 4b. Yorkville 1993 residuals	73

INTRODUCTION

It has long been established that non-methane hydrocarbons play an important role as contributors to ozone and other secondary photochemical pollutants. In the 1950s, Haagen-Smit and his co-workers wrote a classic series of papers which explained the smog problem in Los Angeles, establishing that a major component of photochemical smog was ozone formed from reactions between volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in the presence of sunlight. Since the passage of the 1970 Clean Air Act amendments, regulatory efforts to comply with the National Ambient Air Quality standard for ozone have largely failed [NRC 1991]. Ozone exceedences continue to be a major problem, especially in the southeast region of the United States.

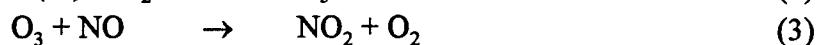
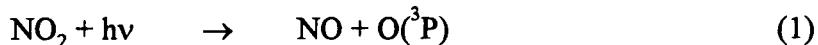
Volatile organic compounds (VOCs) are organic compounds that exist in the vapor phase at standard temperature and pressure. They are significant because they react with oxides of nitrogen to produce ozone, which is a principle constituent of photochemical smog. Hydrocarbons are a subset of VOCs that contain only carbon and hydrogen atoms. In atmospheric chemistry, hydrocarbons are usually referred to as non-methane hydrocarbons because methane is relatively unreactive in the atmosphere (its lifetime with the OH radical is approximately 12 years, assuming a concentration of 7.7×10^5 molecule/cm³)[Vaghjiani and Ravishankara 1991], and is thought to be not important in an air quality perspective.

There are four classifications of hydrocarbons. Alkanes, also called paraffins, are hydrocarbons which contain only single bonds and, as a group, are the generally the least reactive with the OH radical. Alkenes are hydrocarbons with double bonds and are also called olefins. Alkynes are hydrocarbons with triple bonds; of the 60 sampled hydrocarbons in this work, acetylene is the only alkyne. These three groups are collectively called "aliphatics." A fourth classification include the aromatics, or arenes, which have a structural unit based on the benzene ring.

Hydrocarbons are precursors to tropospheric ozone formation. Ozone exists in two different regions of the atmosphere. In the stratosphere at an altitude of about 10

km, high ozone concentrations absorb ultraviolet radiation of 200-300 nm, preventing it from reaching the earth's surface; for this reason, it is called "good ozone". In the troposphere, ozone is a pollution problem because it is a major component of photochemical smog. Excessive ozone concentrations can cause eye and bronchial irritation, respiratory disease, and damage to forests and agriculture [NRC 1991, 31].

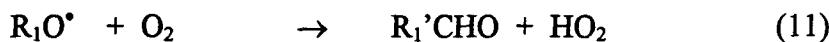
In the troposphere, ozone is produced by the photodissociation of NO₂, as shown in the three step mechanism below. The chemical equations involving the equilibrium of ozone and reactions between NO₂, O₂, O₃ and NO are called the Photostationary State:



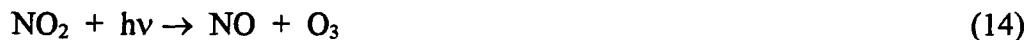
Nitrogen dioxide (NO₂) is photodissociated into nitric oxide (NO) and an excited state of oxygen (O(³P)). The excited oxygen reacts with a diatomic oxygen molecule, producing ozone. However, ozone reacts with nitric oxide, forming NO₂ and O₂, closing the cycle and resulting in no net ozone accumulation.

In the presence of volatile organic compounds, RO₂ radicals are produced by the reaction of the VOCs with OH radicals that also exist in the ambient atmosphere. This competition between RO₂ radicals and O₃ occurs for the oxidation of NO to NO₂. The following set of chemical equations is a simple example of a straight-chain alkane oxidation:





Net:



In this example R_1 and R_2 stand for alkyl groups, R_1' represents an alkyl group with one carbon atom less than R_1 (i.e. $R_1O^\bullet \equiv R_1'CH_2O$). A free radical is a species that contain unpaired electrons (i.e. ROO^\bullet is a peroxy radical [Warneck 1988, 190]). Three major things occur in this reaction sequence. First, a hydrogen atom is abstracted from the alkane by the hydroxyl radical (OH) to form water and an organic radical (equation 4), which combines with O_2 in equation (5) to form the peroxy radical. This peroxy radical reacts with nitric oxide to form NO_2 (eq.6), and NO_2 is photolyzed to produce ozone. The by products of this oxidation include a ketone (R_1COR_2) and an aldehyde (R_1CHO), together called "carbonyls."

The contribution of naturally emitted volatile organic compounds to ozone formation has become of greater concern within the last decade [Lamb et al., 1987; Trainer et al., 1987; Chameides et al., 1988]. Isoprene, α -pinene, β -pinene and limonene are some examples of hydrocarbons emitted by vegetation. Isoprene (2-methyl-1,3-butadiene) is primarily emitted from deciduous trees, while alpha and beta pinene are emitted from coniferous species, which emit three times less than deciduous isoprene emitters, on a unit mass basis [Lamb et al., 1987]. Almost half of the isoprene emitted in the United States is from the Southeast region (48%), while the Northwest accounts for only 3% of emissions [Lamb et al., 1987]. Isoprene emissions are greatest during the summer when temperatures are highest, and minimal in the wintertime. Studies by Tingey [1981] conducted on live oak and slash pine using controlled environmental growth chambers found that temperature increased both isoprene and monoterpene emissions. Tingey also found that isoprene was emitted by the application of simulated daylight, and the emission rate increased with light intensity. Monoterpene emissions were not directly

affected by light. Natural emissions of isoprene, the monoterpenes, and other biogenic VOCs are a concern because of the high reaction rate between these compounds with ozone and the OH radical, and therefore, the strong potential to act as precursors to tropospheric ozone formation. Measurements suggest that isoprene and other biogenics result in high ozone concentrations in urban areas affected by high NO_x concentrations, as well as contributing to relatively high ozone in rural areas [NRC 1991, 8].

Summertime ozone in the South is, on average, among the highest in the United States [SOS 1995, 11]. One reason for this is due to the stagnant conditions during the summer, which inhibit dispersion of pollutants and allows a steady buildup of pollutants and ozone precursors. These stagnating high pressure systems often arise from the stalling of a continental high-pressure system over the Appalachian Mountains [SOS 1993, 12]. Another characteristic which is conducive to high ozone in this region is the dense vegetation, which results in large emissions of isoprene and other natural hydrocarbons [Lamb et al., 1987]. These natural hydrocarbons are highly reactive, and model studies indicate that these natural emissions can significantly affect both urban and rural ozone levels [Chameides et al., 1988; Trainer et al., 1987]. There have been various studies done involving the measurement of background levels of hydrocarbons in the atmosphere of rural continental sites [Jobson et al., 1994; Hov et al., 1991; Colbeck and Harrisson, 1985; Greenberg and Zimmerman, 1984], however, prior to this study, an analysis of rural hydrocarbons in the southeast United States has not been done on a regional scale. In this study, fifty-six non-methane hydrocarbons were analyzed from four rural sites located in the southeastern United States, along with ozone, various trace gases, and meteorological variables. Propylene-equivalent concentrations were calculated to evaluate the contribution of hydrocarbons to ozone, especially the highly reactive biogenic compounds. Relationships between ozone, isoprene and various meteorological parameters were also examined.

SECTION I

REGIONAL CHARACTERIZATION OF NON-METHANE HYDROCARBONS IN THE RURAL SOUTHEAST UNITED STATES

Abstract

Concentrations of non-methane hydrocarbons, as well as ozone, meteorological and trace gas data, were measured at four rural sites located within the southeastern United States as a part of the Southern Oxidants Study. Fifty-six C₂-C₁₀ hydrocarbons were collected from 1200-1300 local time, once every six days from September 1992 through October 1993. The measurements were made in an effort to enhance the understanding of the behavior and trends of ozone and other photochemical oxidants in this region. The light molecular weight alkanes (ethane, propane, n-butane, iso-butane), ethene and acetylene display a seasonal variation of a winter maximum and summer minimum. Isoprene was virtually non-existent during the winter at all sites, and averaged from 9.8 ppbC (Yorkville, GA) to 21.15 ppbC (Centreville, AL) during the summer. The terpene concentration was greatest in the summer with averages ranging 3.19 ppbC (Centreville, AL) to 6.38 ppbC (Oak Grove, MS), but was also emitted during the winter months, with a range of 1.25 to 1.9 ppbC for all sites. Propylene-equivalent concentrations were calculated to account for differences in reaction rates between the hydroxyl radical and individual hydrocarbons, and to thereby estimate their relative contribution to ozone, especially in regards to the highly reactive biogenic compounds such as isoprene. It was calculated that biogenics represent at least 65% of the total non-methane hydrocarbon sum at these four sites during the summer season when considering propylene-equivalent concentrations. An ozone episode which occurred from July 20 to July 24 1993 was used as an example to show ozone profiles at each of the sites, and to show the effect of synoptic meteorology on high ozone by examining NOAA daily weather maps and climatic data. Relationships between meteorological variables such as temperature, relative humidity, solar radiation, and trace gases such as ozone, SO₂, CO

and NO_y were also examined. A multiple regression on ozone at the Yorkville site found temperature, relative humidity and NO_y to be statistically significant, with an R-square of 0.66.

1. Introduction

It has long been established that non-methane hydrocarbons play an important role as precursors to ozone and other secondary photochemical pollutants. Ozone is formed from reactions between volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in the presence of sunlight. Since the passage of the 1970 Clean Air Act amendments, regulatory efforts to comply with the National Ambient Air Quality standard for ozone have been inadequate [NRC 1991, 4; Dimitriades 1989]. Ozone exceedences continue to be a major problem, especially in the southeast region of the United States. Studies have shown that the Southeast is a region where high concentrations of ozone accumulate in both rural and urban areas [SOS 1995, iv]. The contribution of naturally emitted volatile organic compounds to ozone formation in both urban and rural areas has become of greater concern within the last decade [Lamb et al., 1987]. Measurements of biogenically emitted VOCs such as isoprene suggest that these compounds contribute to high ozone concentrations in urban areas affected by NO_x [Trainer et al., 1987; Chameides et al., 1988; NRC 1991, 8]. Various studies have involved measuring isoprene and other ambient hydrocarbon concentrations in rural or remote sites [Andronache et al. 1994; Chameides et al. 1992; Colbeck and Harrisson, 1985; Greenberg and Zimmerman, 1984; Rasmussen and Khalil, 1988; Sexton and Westberg, 1984]. Other studies have reported the seasonal variations of hydrocarbons in continental air [Boudries et al., 1994; Jobson et al., 1994; Hov et al., 1991; Rudolph et al., 1989; Tille et al., 1985].

In this study we (1) compare C₂-C₁₀ hydrocarbons during maximum photochemical activity on a regional scale, (2) analyze the contribution of rural hydrocarbons using propylene-equivalent concentrations, especially in relation to isoprene, and (3) examine the relationship between ozone and reactive nitrogen (NO_y), and between ozone and meteorological variables such as temperature, relative humidity, solar radiation, and ozone.

2. Experiment

2.1. Site Description

The hydrocarbon, trace gas and meteorological data was collected from four rural sites within the SOS-SCION network (Southern Oxidants Study-Southeastern Consortium Intermediate Oxidant Network) located in the southeast United States. The SCION network was established to describe how ozone precursor concentrations vary during the year in different regions of the Southeast. The location of the sites used for this paper include Centreville, Alabama; Oak Grove, Mississippi; Yorkville, Georgia; and Candor, North Carolina. Figure 1 illustrates the location of the sites.

The Centreville site is located in Bibb County, Alabama ($32^{\circ}90'N$, $87^{\circ}23'W$), in a rural area representative of the transitional nature of the region between the lower coastal plain and Appalachian highlands, at an elevation of 136 m mean sea level (msl). Sources of anthropogenic emissions located within a 110 km radius of the sampling site include the cities of Montgomery, Birmingham, and Tuscaloosa. This site is located in a large field approximately 180 m from a NOAA (National Oceanic and Atmospheric Administration) weather radar station.

The Oak Grove site ($30^{\circ}99'N$, $88^{\circ}93'W$) is located in the Desoto National Forest in Perry County, Mississippi at an elevation 85 m msl. This site is located in a rural area representative of the lower coastal plain. It is moderately forested with a canopy at approximately 12 m, and predominantly consists of conifers. The forested areas are interspersed with cultivated farm land. The site is located in a large field approximately 46 m from the nearest row of brush and 152 m from the intersection of two dirt roads. The area immediately surrounding the site is mowed on a regular basis and is surrounded by cultivated farm land. The nearest residence visible from the site is located approximately a quarter of one mile away. It is situated off of state route 29 and approximately 40 km southeast of Hattiesburg, Mississippi.



Figure 1. Map of sampling sites

The Yorkville site ($33^{\circ}55'41''N$, $85^{\circ}02'46''W$) is located in Paulding County, Georgia, at an elevation approximately 400 m above sea level. The site is situated in a rural area representative of the southern highlands, consisting of hardwood forests interspersed with open pasture and tilled farmland. The site is off route 278 and is approximately 72 km west of Atlanta, and 48 km west of a power generating station.

The Candor site ($35.26^{\circ}N$, $79.84^{\circ}W$, 197 m msl elevation) is located in the Central Piedmont region of North Carolina on the eastern border of the Uwharrie National Forest. The sampling site is located in an open field approximately 1200 m^2 , and the field is surrounded by forests mixed with deciduous and coniferous trees. Sources of anthropogenic pollution located within a 120 km radius of the sampling site include the urban areas of Raleigh-Durham, Greensboro, Winston-Salem, and the junction between I-40 and I-85, which are all situated to the north and northeast of the site.

2.2. Data Collection and Analysis

The hydrocarbon data used in this paper was sampled from September 1992 through October 1993, and includes data sampled during June 1992 at the Candor site. The Centreville and Candor sites each include 49 total observations; Oak Grove and Yorkville include 61 and 55 observations, respectively. The sampling days used for the seasonal averages at each site are listed at the end of Tables 1a-d. Time integrated air samples were collected in 6 liter SUMMA electropolished stainless steel canisters from 1200 to 1300 local time, once every six days. This sampling frequency was chosen so that each day of the week would be represented in the study. The hydrocarbon samples were collected in evacuated canisters by opening the canister and allowing the internal pressure to reach ambient pressure. C₂-C₁₀ hydrocarbons were analyzed at the University of Miami using a Hewlett Packard HP 5890II gas chromatograph equipped with a cryogenic cooling option and flame ionization detection. Data reduction was accomplished using HP 3365 Chemstation II software on PC-DOS based personal computers. The automatic air concentrator used was a modified Entech 2000 (Entech Laboratory Automation, Simi Valley, CA). The detection limit was 0.1 ppbC (parts per billion carbon) with a

reproducibility of 30%. A detailed description of the GC analysis is published elsewhere [Farmer et al., 1994].

Measurements of NO, NO_y (the sum of the reactive odd nitrogen species, NO_y = NO + NO₂ + organic nitrates + inorganic nitrates), SO₂, CO, and O₃ as well as meteorological parameters such as temperature, relative humidity, solar radiation, barometric pressure, and wind speed and direction were made every day at fifteen minute intervals throughout the year. NO and NO_y were measured with the TECO 42S (Thermo Environmental Instruments Inc.) chemiluminescent high sensitivity analyzer. For the Centreville, Oak Grove and Yorkville sites, air samples for the continuous gas monitoring equipment, excluding the non-methane hydrocarbons, were collected through 0.25" teflon tubing, each instrument equipped with a dedicated teflon line and particulate filter located at the intake. The NO_y converter for the TECO 42S was located within the intake dome and operated at 350°C. Cylinders containing gas standards for NO, NO_y, SO₂ and CO were present along with a TECO 146 dynamic gas calibrator to provide for calibration and zero and span checks. The site was equipped with a zero air generating system. Zero air for the O₃, NO/NO_y and SO₂ monitors was generated by passing ambient air through a series of canisters containing purafill, activated charcoal and brominated charcoal. Zero air for the CO monitor was generated by passing ambient air through a palladium converter. The trace gas (except ozone) and meteorological data used for this work was an average of the 1200-1300 data from the corresponding hydrocarbon sampling days. The daily maximum value was used for ozone, which generally occurred mid-afternoon (~1500). The data used for the multiple regression analysis, including CO, SO₂, NO_y and ozone, plus the meteorological variables, consisted of daily averages of the 1000-1600 period from June 1 1993 to August 31 1993 (92 observations).

3. Results and Discussion

3.1. Measurements of C₂-C₁₀ Speciated Hydrocarbons

Tables 1a-d summarize the seasonal average, median, standard deviation and range of the fifty-six C₂-C₁₀ compounds sampled at each site. Isobutene and 1-butene were added together because of problems with coelution, as well as m-xylene and p-xylene. For the most part, the autumn through summer seasons represent the data in chronological order: autumn is associated with September through November 1992, winter includes December 1992 through February 1993, spring includes March through May 1993, and summer includes June through August 1993. However, the autumn category also includes sampling days from September and October 1993, and the summer category includes three days from June 1992 at the Candor site. The sampling days used for the seasonal averages are listed at the end of Tables 1a-d.

During the wintertime, all sites had the same top four dominant compounds in the following order: propane, n-butane, ethane, and isopentane, with the exception of the Yorkville site, which had isopentane and ethane switched around in ranking. The compounds following the ones listed above were within the top 10 most abundant species: acetylene, n-pentane, ethene, isobutane, and benzene. Toluene was also within the top 10 at all sites except at Oak Grove, where it ranked 11th. The individual C₂-C₅ alkanes (except cyclopentane) dominated the list of most abundant compounds for all four sites during the winter. During the summer, the 10 most abundant compounds were highly variable among the sites. Isoprene was the dominant hydrocarbon during the summer at all but the Oak Grove site, where n-pentane was the most abundant hydrocarbon (16.51 ± 20.97 ppbC, median = 7.68 ppbC) with isoprene immediately following with a concentration of 11 ± 4.2 ppb. The compounds isoprene, propane, isopentane, 2-methylpentane, and styrene consistently appeared in the top 10 most abundant hydrocarbons among all four sites, though not necessarily in that order.

Figures 2-4 shows the seasonal averages of various compounds and compound sums for each site. In Figure 2, ethane, propane, n-butane, isobutane, ethene and acetylene display a distinct seasonal variation with maximums occurring during the winter.

Table 1a. Seasonal averages of hydrocarbon compound concentrations in ppbC at Centreville, Alabama

Compound	Autumn						Winter						Spring						Summer					
	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max
Ethene	0.88	0.76	0.69	2.46	0.00	1.98	2.03	0.55	2.69	1.09	1.92	1.78	1.17	4.79	0.59	0.61	0.54	0.60	1.57	0.00				
Acetylene	1.06	0.92	1.00	3.46	0.00	2.21	2.13	0.50	3.48	1.44	1.08	0.70	1.02	2.45	0.00	0.36	0.32	0.39	1.09	0.00				
Ethane	3.11	2.62	2.98	10.50	0.00	3.30	2.76	1.60	7.39	0.96	1.31	1.16	1.29	3.71	0.00	1.74	1.04	1.88	4.82	0.00				
Propene	0.66	0.67	0.26	1.21	0.27	0.78	0.70	0.21	1.20	0.52	0.60	0.50	0.34	1.20	0.15	0.73	0.47	0.79	2.89	0.22				
Propane	4.22	2.73	3.50	12.02	1.22	8.40	6.48	4.25	15.36	4.08	4.25	3.50	2.87	10.82	1.00	2.60	2.81	1.94	6.97	0.26				
Isobutane	1.03	0.61	0.92	3.25	0.22	1.95	1.50	1.07	4.05	0.96	0.89	0.66	0.69	2.15	0.12	0.77	0.77	0.56	2.16	0.10				
Isobutene + 1-Butene	1.07	0.89	0.53	2.24	0.44	1.16	1.19	0.86	2.70	0.00	1.07	0.91	0.95	2.67	0.15	1.55	0.93	1.01	3.46	0.48				
n-Butane	2.18	1.51	1.77	6.41	0.50	4.92	3.80	2.54	9.84	2.17	1.96	1.48	1.39	5.18	0.38	1.48	1.29	0.76	3.39	0.50				
Trans-2-butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cis-2-butene	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.06	0.21	0.00	0.02	0.00	0.07	0.22	0.00	0.04	0.00	0.11	0.36	0.00				
3-methyl-1-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.10	0.00				
Isopentane	1.53	1.08	1.05	3.51	0.39	3.25	2.45	2.06	9.08	1.31	2.78	1.51	3.10	10.77	0.54	2.22	2.23	1.09	4.09	0.66				
1-Pentene	0.26	0.17	0.30	0.81	0.00	0.49	0.39	0.49	1.88	0.00	0.44	0.37	0.31	1.10	0.00	0.36	0.32	0.18	0.60	0.15				
2-methyl-1-Butene	0.04	0.00	0.08	0.26	0.00	0.01	0.00	0.05	0.18	0.00	0.04	0.00	0.06	0.15	0.00	0.08	0.00	0.11	0.25	0.00				
n-Pentane	1.04	0.66	0.82	2.78	0.29	2.00	1.61	1.09	4.00	0.95	0.90	0.61	0.64	2.27	0.25	1.04	0.74	0.78	2.98	0.42				
Isoprene	2.65	1.62	3.08	9.19	0.00	0.07	0.00	0.26	0.95	0.00	2.09	0.21	3.39	8.76	0.00	21.15	19.37	10.20	43.45	8.26				
Trans-2-pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.16	0.52	0.00	0.15	0.14	0.15	0.49	0.00				
Cis-2-pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.10	0.00				
2-methyl-2-Butene	0.03	0.00	0.05	0.14	0.00	0.05	0.00	0.07	0.18	0.00	0.05	0.00	0.07	0.18	0.00	0.06	0.00	0.11	0.29	0.00				
3-methyl-1-Pentene	0.31	0.14	0.40	1.20	0.00	0.05	0.00	0.14	0.49	0.00	0.28	0.14	0.36	0.97	0.00	0.52	0.00	0.84	2.03	0.00				
4-methyl-1-Pentene	0.10	0.11	0.10	0.27	0.00	0.14	0.15	0.13	0.37	0.00	0.18	0.18	0.10	0.36	0.00	0.11	0.13	0.10	0.26	0.00				
Cyclopentane	0.10	0.10	0.07	0.26	0.00	0.20	0.17	0.06	0.31	0.11	0.08	0.11	0.07	0.20	0.00	0.05	0.00	0.09	0.25	0.00				
2-Methylpentane	0.64	0.35	0.90	3.69	0.13	0.80	0.64	0.47	1.76	0.32	1.20	0.39	1.68	5.89	0.12	3.34	3.51	1.93	6.38	0.17				
3-Methylpentane	0.50	0.41	1.41	0.00	0.89	0.95	0.29	1.37	0.41	0.67	0.53	0.38	1.26	0.24	0.82	0.80	0.36	1.36	0.30					
n-Hexane	0.39	0.25	0.31	1.08	0.11	0.72	0.59	0.37	1.54	0.32	0.34	0.29	0.26	1.04	0.13	0.68	0.38	0.57	1.90	0.23				
Cis-3-hexene	0.07	0.00	0.10	0.28	0.00	0.01	0.00	0.03	0.11	0.00	0.10	0.00	0.13	0.35	0.00	0.70	0.60	0.45	1.62	0.25				
Methylcyclopentane	0.11	0.00	0.14	0.47	0.00	0.34	0.31	0.15	0.66	0.16	0.14	0.12	0.15	0.43	0.00	0.19	0.14	0.24	0.81	0.00				
2,4-Dimethylpentane	0.07	0.00	0.08	0.24	0.00	0.14	0.15	0.06	0.21	0.00	0.10	0.00	0.13	0.34	0.00	0.29	0.16	0.41	1.40	0.00				
1,1,1-Trichloroethane	0.40	0.35	0.14	0.81	0.29	0.42	0.41	0.07	0.59	0.32	0.43	0.42	0.11	0.71	0.26	0.43	0.41	0.05	0.51	0.35				
Benzene	0.87	0.81	0.39	1.72	0.31	1.36	1.32	0.26	1.83	0.97	0.79	0.65	0.33	1.48	0.42	0.61	0.54	0.23	0.98	0.33				
Cyclohexane	0.06	0.00	0.08	0.25	0.00	0.18	0.14	0.12	0.36	0.00	0.08	0.11	0.08	0.21	0.00	0.15	0.16	0.41	1.40	0.00				
2,3-Dimethylpentane	0.57	0.49	0.39	1.72	0.12	0.35	0.32	0.10	0.62	0.18	0.67	0.55	0.54	1.71	0.00	0.86	0.71	0.41	1.50	0.36				
Trichloroethylene	0.16	0.13	0.10	0.34	0.00	0.28	0.19	0.16	0.59	0.10	0.17	0.14	0.13	0.45	0.00	0.24	0.23	0.11	0.44	0.10				
Methylcyclohexane	0.30	0.20	0.36	1.49	0.00	0.28	0.26	0.12	0.47	0.13	0.18	0.24	0.16	0.39	0.00	0.42	0.45	0.14	0.63	0.23				

Table 1a. Seasonal averages of hydrocarbon compound concentrations in ppbC at Centreville, Alabama

Compound	Autumn				Winter				Spring				Summer																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						
	Mean	Medn	Std	Max	Mean	Medn	Std	Max	Mean	Medn	Std	Max	Mean	Medn	Std	Max																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
2,3,4-Trimethylpentane	0.07	0.00	0.09	0.26	0.00	0.08	0.10	0.07	0.19	0.00	0.04	0.00	0.16	0.00	0.03	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
Toluene	1.08	0.70	0.90	3.61	0.39	1.86	1.60	1.41	6.25	0.67	0.88	0.84	0.53	2.26	0.25	1.20																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
n-Octane	0.15	0.12	0.13	0.49	0.00	0.18	0.17	0.06	0.32	0.10	0.11	0.12	0.13	0.07	0.12	0.20																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
Perchloroethylene	0.13	0.00	0.41	1.61	0.00	0.00	0.00	0.00	0.04	0.00	0.04	0.00	0.11	0.38	0.00	0.01																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
Ethylbenzene	0.21	0.13	0.22	0.86	0.00	0.26	0.25	0.09	0.46	0.11	0.15	0.15	0.14	0.45	0.00	0.20																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
m+p Xylene	0.43	0.27	0.61	2.45	0.00	0.52	0.52	0.27	1.20	0.00	1.45	0.26	3.76	12.74	0.00	0.40																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
Styrene	0.78	0.64	0.58	2.23	0.26	0.51	0.49	0.37	1.52	0.00	1.22	1.11	0.95	3.50	0.20	1.27																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
o-Xylene	0.17	0.12	0.24	0.91	0.00	0.23	0.25	0.13	0.55	0.00	0.17	0.14	0.13	0.52	0.00	0.14																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
Isopropylbenzene	0.07	0.00	0.10	0.27	0.00	0.12	0.11	0.12	0.37	0.00	0.32	0.11	0.68	2.29	0.00	0.07																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
a-Pinene	0.73	0.49	0.67	2.23	0.00	0.36	0.32	0.26	0.70	0.00	0.53	0.43	0.41	1.44	0.00	1.60																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
n-Propylbenzene	0.09	0.10	0.10	0.25	0.00	0.06	0.00	0.08	0.23	0.00	0.18	0.16	0.16	0.54	0.00	0.15																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
1-Ethyl-3-Methylbenzene	0.13	0.10	0.18	0.67	0.00	0.15	0.14	0.11	0.42	0.00	0.12	0.11	0.16	0.51	0.00	0.19																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
1-Ethyl-4-Methylbenzene	0.26	0.28	0.13	0.48	0.00	0.29	0.25	0.16	0.67	0.16	0.24	0.22	0.19	0.62	0.00	0.28																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
1,3,5-Trimethylbenzene	0.21	0.21	0.11	0.38	0.00	0.18	0.15	0.16	0.53	0.00	0.31	0.34	0.16	0.53	0.00	0.19																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
1-Ethyl-2-Methylbenzene	0.17	0.17	0.09	0.36	0.00	0.23	0.25	0.09	0.38	0.10	0.15	0.14	0.10	0.33	0.00	0.23																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
p-Pinene	0.61	0.39	0.61	2.44	0.18	0.46	0.46	0.21	0.80	0.19	1.23	0.90	1.19	4.40	0.22	1.36																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
1,2,4-Trimethylbenzene	0.32	0.22	0.20	0.85	0.10	0.36	0.24	0.32	1.28	0.15	0.66	0.44	0.56	2.00	0.12	0.73																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
Limonene	0.33	0.23	0.32	1.34	0.00	0.43	0.31	0.24	0.85	0.27	0.54	0.25	0.51	1.47	0.15	0.24																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
1,3-Diethylbenzene	0.44	0.33	0.59	2.50	0.00	0.93	0.86	0.53	2.18	0.15	0.69	0.39	0.70	2.47	0.20	0.70																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
n-Butylbenzene	0.18	0.20	0.15	0.45	0.00	0.24	0.20	0.18	0.62	0.00	0.28	0.21	0.22	0.76	0.13	0.29																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
Sampling days used for seasonal averages	9/3/1992	9/10/1993	9/15/1992	9/22/1993	10/3/1992	10/9/1992	10/15/1992	10/21/1992	10/27/1992	11/2/1992	11/8/1992	11/14/1992	11/20/1992	11/26/1992	12/2/1992	12/8/1992	12/14/1992	12/20/1992	12/26/1992	1/1/1993	1/7/1993	1/13/1993	1/19/1993	1/25/1993	5/7/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/1993	6/7/1993	6/13/1993	6/19/1993	6/25/1993	7/18/1993	7/27/1993	8/5/1993	8/23/1993	8/29/1993	9/3/1993	9/10/1993	9/15/1993	9/22/1993	3/8/1993	3/20/1993	3/26/1993	4/13/1993	4/17/1993	4/19/1993	4/25/1993	5/19/1993	5/25/1993	6/1/19

Table 1b. Seasonal averages of hydrocarbon compound concentrations in ppbC at Oak Grove, Mississippi

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	StdDev	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min
Ethene	1.07	1.00	0.55	2.40	0.14	1.58	1.42	0.88	3.71	0.60	1.72	1.62	1.27	4.60	0.00	0.57	0.68	0.52	1.62	0.00
Acetylene	1.23	0.78	1.16	4.84	0.25	1.98	1.92	0.74	3.76	0.88	1.08	1.23	1.03	3.46	0.00	0.45	0.06	0.72	2.17	0.00
Ethane	3.27	2.73	2.23	8.96	0.76	3.43	2.30	2.56	10.35	0.00	1.93	1.25	2.30	6.67	0.00	1.02	0.72	1.25	3.79	0.00
Propene	0.87	0.74	0.50	2.61	0.36	0.56	0.55	0.20	0.94	0.22	0.49	0.40	0.27	1.29	0.26	0.61	0.59	0.29	1.19	0.00
Propane	4.09	3.08	3.53	13.64	0.17	8.07	6.09	6.09	23.34	2.38	3.86	3.66	2.29	9.83	0.85	4.04	1.28	5.61	17.85	0.79
Isobutane	1.13	0.79	0.84	3.07	0.25	2.29	1.72	1.25	4.85	1.18	1.04	1.04	0.55	2.01	0.19	1.25	1.34	0.92	2.74	0.00
Isobutene + 1-Butene	2.94	2.05	2.96	12.76	0.28	0.98	1.08	0.57	2.12	0.10	1.27	0.99	1.17	5.22	0.30	1.54	1.44	0.64	3.08	0.54
n-Butane	2.28	1.71	1.75	7.31	0.64	5.52	4.17	3.24	12.23	2.46	2.25	1.81	1.37	4.72	0.38	1.87	1.82	0.85	3.37	0.40
Trans-2-butene	0.01	0.00	0.02	0.10	0.00	0.02	0.00	0.04	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.09	0.00
Cis-2-butene	0.02	0.00	0.08	0.34	0.00	0.02	0.00	0.07	0.26	0.00	0.02	0.00	0.04	0.13	0.00	0.17	0.00	0.25	0.71	0.00
3-methyl-1-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopentane	1.55	1.38	0.89	3.76	0.46	2.76	2.36	1.52	5.74	1.25	1.81	1.56	1.15	5.61	0.58	5.90	4.82	4.42	14.89	1.50
1-Pentene	0.28	0.05	0.46	1.72	0.00	0.41	0.09	0.55	1.81	0.00	0.29	0.20	0.38	1.44	0.00	0.66	0.35	0.79	3.08	0.19
2-methyl-1-Butene	0.04	0.00	0.09	0.29	0.00	0.02	0.00	0.07	0.28	0.00	0.06	0.00	0.08	0.25	0.00	0.12	0.00	0.18	0.51	0.00
n-Pentane	0.95	0.75	0.62	2.84	0.29	1.92	1.49	1.12	4.47	0.93	0.89	0.82	0.49	2.18	0.23	16.51	7.68	20.97	58.05	0.88
Isoprene	2.65	0.97	2.95	9.97	0.00	0.06	0.00	0.17	0.65	0.00	1.69	0.38	3.53	14.02	0.00	11.19	10.93	4.20	18.09	3.07
Trans-2-pentene	0.08	0.00	0.22	0.88	0.00	0.02	0.00	0.07	0.25	0.00	0.07	0.00	0.13	0.38	0.00	0.38	0.34	0.36	1.15	0.00
Cis-2-pentene	0.01	0.00	0.04	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.04	0.14	0.00	0.07	0.00	0.09	0.24	0.00
2-methyl-2-Butene	0.08	0.00	0.12	0.42	0.00	0.07	0.00	0.11	0.30	0.00	0.04	0.00	0.09	0.29	0.00	0.10	0.11	0.09	0.25	0.00
3-methyl-1-Pentene	0.27	0.13	0.33	1.27	0.00	0.03	0.00	0.11	0.41	0.00	0.31	0.29	0.34	0.93	0.00	1.31	1.25	0.76	2.84	0.00
4-methyl-1-Pentene	0.08	0.00	0.12	0.44	0.00	0.16	0.19	0.14	0.43	0.00	0.22	0.19	0.14	0.64	0.00	0.11	0.13	0.09	0.26	0.00
Cyclopentane	0.10	0.12	0.08	0.22	0.00	0.18	0.15	0.08	0.39	0.12	0.08	0.10	0.08	0.22	0.00	0.16	0.14	0.16	0.42	0.00
2-Methylpentane	0.72	0.45	0.67	2.52	0.14	0.77	0.60	0.48	1.76	0.28	1.25	0.69	1.14	3.54	0.00	2.16	2.14	0.97	3.57	0.57
3-Methylpentane	0.58	0.49	0.34	1.22	0.00	0.97	0.91	0.45	2.00	0.39	0.87	0.71	0.50	2.04	0.41	0.93	0.84	0.42	1.91	0.42
n-Hexane	0.44	0.37	0.29	1.23	0.10	0.80	0.52	0.49	1.73	0.33	0.40	0.42	0.16	0.72	0.13	0.72	0.80	0.37	1.16	0.15
Cis-3-hexene	0.09	0.05	0.11	0.31	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.12	0.30	1.03	0.00	0.48	0.44	0.25	1.01	0.14
Methylcyclopentane	0.15	0.13	0.12	0.45	0.00	0.34	0.22	0.23	0.82	0.16	0.39	0.19	0.55	2.34	0.00	0.62	0.40	0.87	3.30	0.10
2,4-Dimethylpentane	0.15	0.15	0.14	0.41	0.00	0.16	0.13	0.15	0.54	0.00	0.12	0.13	0.09	0.27	0.00	0.25	0.22	0.19	0.81	0.00
1,1,1-Trichloroethane	0.37	0.33	0.13	0.84	0.26	0.39	0.40	0.05	0.50	0.31	0.52	0.46	0.36	1.82	0.28	0.63	0.52	0.37	1.75	0.40
Benzene	0.78	0.67	0.34	1.55	0.33	1.36	1.29	0.41	2.30	0.69	0.90	0.97	0.32	1.39	0.32	0.69	0.69	0.24	1.05	0.17
Cyclohexane	0.09	0.00	0.13	0.42	0.00	0.16	0.12	0.17	0.60	0.00	0.10	0.07	0.11	0.35	0.00	1.31	0.35	3.31	11.80	0.00
2,3-Dimethylpentane	0.62	0.44	0.58	2.08	0.00	0.41	0.31	0.24	0.84	0.10	0.68	0.58	0.47	2.13	0.09	0.80	0.73	0.27	1.28	0.40
Trichloroethylene	0.24	0.20	0.17	0.64	0.00	0.30	0.25	0.15	0.56	0.12	0.26	0.20	0.18	0.60	0.00	0.24	0.23	0.15	0.60	0.00
Methylcyclohexane	0.47	0.38	0.37	1.33	0.00	0.29	0.23	0.19	0.83	0.11	0.28	0.30	0.20	0.81	0.00	0.69	0.60	0.45	1.99	0.30

Table 1b. Seasonal averages of hydrocarbon compound concentrations in ppbC at Oak Grove, Mississippi

Compound	Autumn						Winter						Spring						Summer																														
	Mean		Medn		StDev		Max		Min		Mean		Medn		StDev		Max		Min		Mean		Medn		StDev		Max		Min																				
	2,3,4-Trimethylpentane	0.14	0.11	0.16	0.48	0.00	0.08	0.10	0.08	0.26	0.00	0.06	0.00	0.10	0.37	0.00	0.15	0.06	0.23	0.62	0.00	Toluene	0.90	0.90	0.30	1.40	0.33	1.25	1.08	0.68	2.93	0.45	0.89	0.91	0.43	2.00	0.22	3.63	2.44	4.10	15.56	0.56							
n-Octane	0.28	0.20	0.22	0.96	0.13	0.15	0.14	0.08	0.29	0.00	0.13	0.13	0.11	0.40	0.00	0.30	0.28	0.11	0.47	0.12	Ethylbenzene	0.07	0.00	0.10	0.29	0.00	0.03	0.00	0.07	0.24	0.00	0.41	0.05	1.23	5.00	0.00	0.09	0.04	0.11	0.33	0.00								
m+p Xylene	0.58	0.46	0.44	1.97	0.14	0.74	0.44	1.05	4.44	0.17	0.33	0.34	0.26	8.80	0.00	0.89	0.72	0.50	1.93	0.13	Styrene	1.06	1.12	0.65	2.38	0.00	0.51	0.43	0.30	1.26	0.22	1.09	1.02	0.78	3.65	0.19	2.45	1.68	1.80	6.69	1.05								
o-Xylene	0.26	0.22	0.18	0.67	0.00	0.20	0.18	0.10	0.39	0.00	0.10	0.00	0.12	0.31	0.00	0.36	0.29	0.19	0.75	0.12	Isopropylbenzene	0.18	0.11	0.22	0.69	0.00	0.12	0.11	0.10	0.46	0.12	0.20	0.19	0.10	3.37	0.00	0.45	0.37	0.19	0.77	0.20								
a-Pinene	1.24	0.97	0.84	3.20	0.31	0.50	0.37	0.43	1.41	0.00	1.84	1.31	1.55	5.98	0.23	2.71	2.68	1.20	5.00	1.08	n-Propylbenzene	0.23	0.18	0.19	0.72	0.00	0.07	0.09	0.07	0.18	0.00	0.34	0.30	0.37	1.59	0.00	0.31	0.22	0.21	0.79	0.15								
1-Ethyl-3-Methylbenzene	0.28	0.23	0.24	0.88	0.00	0.13	0.14	0.11	0.31	0.00	0.11	0.06	0.16	0.62	0.00	0.28	0.23	0.24	0.84	0.00	1-Ethyl-4-Methylbenzene	0.52	0.38	0.39	1.64	0.13	0.43	0.39	0.28	1.37	0.18	0.35	0.30	0.20	0.93	0.00	0.65	0.51	0.47	2.07	0.30								
1,3,5-Trimethylbenzene	0.48	0.32	0.44	1.90	0.00	0.15	0.16	0.13	0.48	0.00	0.20	0.12	0.28	1.13	0.00	0.43	0.23	0.52	1.58	0.12	1-Ethyl-2-Methylbenzene	0.32	0.21	0.27	1.12	0.00	0.21	0.23	0.09	0.36	0.10	0.19	0.18	0.15	0.57	0.00	0.45	0.50	0.19	0.81	0.16								
b-Pinene	1.47	1.08	1.11	3.54	0.17	0.67	0.53	0.41	1.78	0.30	1.77	1.54	1.28	4.52	0.25	3.04	2.49	1.67	6.14	1.25	1,2,4-Trimethylbenzene	0.61	0.29	0.72	2.85	0.11	0.54	0.35	0.46	1.35	0.10	0.83	0.75	0.48	2.23	0.20	0.72	0.67	0.61	2.34	0.18								
Limonene	0.48	0.35	0.39	1.49	0.00	0.53	0.47	0.22	1.00	0.21	0.41	0.27	0.26	0.89	0.18	0.63	0.45	0.42	1.46	0.25	1,3-Diethylbenzene	0.53	0.43	0.34	1.12	0.09	1.45	1.21	2.10	8.72	0.09	0.82	0.44	1.26	5.34	0.15	1.16	0.37	1.62	4.04	0.00								
n-Butylbenzene	0.41	0.27	0.43	1.38	0.00	0.30	0.28	0.16	0.66	0.13	0.35	0.17	0.32	1.10	0.00	0.42	0.37	0.32	1.25	0.13	Sampling days used for seasonal averages	9/2/1992	11/20/1992	12/2/1992	2/12/1993	3/2/1993	5/13/1993	6/6/1993	9/9/1992	11/26/1992	12/8/1992	2/18/1993	3/8/1993	5/19/1993	6/12/1993	9/21/1992	9/4/1993	9/27/1992	9/10/1993	12/20/1992	12/26/1992	1/1/1993	1/7/1993	1/13/1993	1/19/1993	1/25/1993	1/31/1993	2/6/1993	11/14/1992

Sampling days used for seasonal averages

Table 1c. Seasonal averages of hydrocarbon compound concentrations in ppbC at Yorkville, Georgia

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min
Ethene	1.05	1.01	0.61	2.06	0.00	2.85	2.58	1.70	6.56	0.87	1.37	0.99	0.91	2.70	0.22	0.90	0.49	1.17	4.05	0.00
Acetylene	1.16	1.12	0.96	3.85	0.00	3.16	2.67	1.96	8.08	1.52	1.55	1.16	1.56	3.83	0.00	0.72	0.66	0.43	1.25	0.00
Ethane	2.41	2.37	1.30	4.69	0.00	3.75	3.36	1.86	7.70	1.84	1.54	1.18	1.90	6.28	0.00	0.96	0.65	0.96	3.61	0.18
Propene	0.81	0.67	0.60	2.69	0.20	1.09	0.74	0.73	2.90	0.47	1.50	0.66	2.37	8.76	0.21	1.61	0.99	2.10	7.12	0.00
Propane	4.07	3.18	3.12	14.24	0.50	8.01	6.59	4.03	17.45	4.27	4.38	2.96	4.56	18.01	0.23	1.89	2.21	1.28	3.80	0.13
Isobutane	0.97	0.79	0.73	2.45	0.16	2.42	1.51	2.36	9.52	0.99	0.96	0.84	0.72	2.45	0.14	0.91	0.67	1.19	4.15	0.00
Isobutene+1-Butene	3.02	1.67	2.97	7.78	0.15	1.26	0.77	1.34	5.23	0.17	0.84	0.97	0.66	2.47	0.12	1.16	1.06	0.63	2.10	0.00
n-Butane	2.41	1.90	1.72	7.33	0.70	6.91	4.89	6.24	21.34	2.45	2.48	1.16	2.80	11.12	0.81	1.96	1.64	1.23	4.67	0.75
Trans-2-butene	0.01	0.00	0.03	0.11	0.00	0.04	0.00	0.09	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cis-2-butene	0.01	0.00	0.04	0.16	0.00	0.04	0.00	0.10	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.21	0.68	0.00
3-methyl-1-Butene	0.01	0.00	0.03	0.11	0.00	0.03	0.00	0.07	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.08	0.19	0.00
Isopentane	2.69	1.88	1.97	7.51	0.52	4.93	2.65	6.47	24.42	1.15	3.84	1.94	5.25	20.44	0.62	5.02	2.73	6.40	21.88	0.00
1-Pentene	0.33	0.35	0.27	0.85	0.00	0.31	0.13	0.46	1.60	0.00	0.25	0.23	0.22	0.84	0.00	1.91	0.39	3.11	10.06	0.32
2-methyl-1-Butene	0.40	0.09	1.16	5.00	0.00	0.10	0.00	0.19	0.52	0.00	0.07	0.00	0.10	0.27	0.00	0.19	0.14	0.24	0.72	0.00
n-Pentane	1.75	1.16	1.52	6.36	0.26	3.05	1.53	3.66	13.88	0.82	1.68	0.83	2.01	7.62	0.30	2.15	1.06	2.28	7.61	0.19
Isoprene	1.73	0.65	2.18	8.13	0.00	0.04	0.00	0.07	0.21	0.00	2.41	0.58	5.01	18.38	0.00	9.80	9.02	2.39	13.53	6.40
Trans-2-pentene	0.10	0.00	0.18	0.60	0.00	0.10	0.00	0.22	0.65	0.00	0.45	0.14	0.85	3.06	0.00	1.44	0.17	3.82	12.28	0.00
Cis-2-pentene	0.02	0.00	0.07	0.29	0.00	0.06	0.00	0.13	0.36	0.00	0.05	0.00	0.16	0.59	0.00	0.07	0.00	0.16	0.51	0.00
2-methyl-2-Butene	0.08	0.03	0.13	0.56	0.00	0.14	0.00	0.23	0.67	0.00	0.82	0.00	2.34	8.43	0.00	0.19	0.06	0.28	0.81	0.00
3-methyl-1-Pentene	0.25	0.15	0.31	0.99	0.00	0.10	0.05	0.13	0.38	0.00	0.45	0.16	0.60	1.91	0.00	1.79	1.84	1.23	3.68	0.00
4-methyl-1-Pentene	0.07	0.00	0.10	0.35	0.00	0.09	0.00	0.12	0.32	0.00	0.17	0.16	0.16	0.58	0.00	0.26	0.13	0.46	1.52	0.00
Cyclopentane	0.15	0.14	0.09	0.36	0.00	0.25	0.19	0.19	0.81	0.14	0.12	0.11	0.10	0.27	0.00	0.19	0.08	0.26	0.65	0.00
2-Methylpentane	0.68	0.52	0.47	1.62	0.16	1.21	0.81	1.07	3.49	0.31	1.63	1.65	1.63	6.20	0.13	3.92	3.38	3.17	9.18	0.14
3-Methylpentane	0.78	0.72	0.47	1.76	0.16	1.04	0.78	0.69	2.44	0.34	0.66	0.57	0.36	1.30	0.13	1.05	0.77	0.77	2.77	0.25
n-Hexane	0.51	0.42	0.29	1.07	0.13	0.96	0.69	0.72	2.79	0.36	0.42	0.38	0.30	1.27	0.00	0.68	0.38	0.75	2.64	0.00
Cis-3-hexene	0.05	0.00	0.07	0.21	0.00	0.03	0.00	0.06	0.15	0.00	0.14	0.00	0.17	0.44	0.00	0.72	0.35	1.11	3.82	0.14
Methylcyclopentane	0.24	0.22	0.16	0.55	0.00	0.48	0.35	0.40	1.53	0.18	0.31	0.22	0.32	1.31	0.10	0.29	0.16	0.37	1.30	0.00
2,4-Dimethylpentane	0.15	0.13	0.15	0.50	0.00	0.25	0.18	0.23	0.67	0.00	0.13	0.14	0.09	0.30	0.00	0.43	0.25	0.44	1.22	0.00
1,1,1-Trichloroethane	0.43	0.39	0.12	0.71	0.30	0.45	0.36	0.23	0.99	0.28	0.77	0.48	0.90	3.66	0.27	0.64	0.49	0.36	1.55	0.31
Benzene	0.98	0.89	0.51	2.35	0.40	1.79	1.65	0.99	4.46	0.97	0.92	0.77	0.38	1.94	0.57	1.22	0.91	0.93	3.57	0.41
Cyclohexane	0.16	0.00	0.38	1.59	0.00	0.28	0.14	0.59	2.21	0.00	0.12	0.14	0.11	0.38	0.00	1.00	0.25	1.63	4.93	0.00
2,3-Dimethylpentane	0.39	0.39	0.20	0.82	0.00	0.54	0.38	0.38	1.32	0.21	0.58	0.57	0.38	1.32	0.00	1.11	1.03	0.55	2.45	0.49
Trichloroethylene	0.23	0.18	0.18	0.73	0.00	0.37	0.33	0.22	0.78	0.10	0.29	0.16	0.25	0.93	0.12	0.18	0.15	0.14	0.39	0.00
Methylcyclohexane	0.23	0.20	0.17	0.72	0.00	0.39	0.25	0.35	1.29	0.12	0.30	0.32	0.24	0.89	0.00	0.57	0.38	0.38	1.40	0.20

Table 1c. Seasonal averages of hydrocarbon compound concentrations in ppbC at Yorkville, Georgia

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	SD	Max	Min	Mean	Medn	SD	Max	Min	Mean	Medn	SD	Max	Min	Mean	Medn	SD	Max	Min
2,3,4-Trimethylpentane	0.14	0.09	0.16	0.51	0.00	0.25	0.15	0.31	0.99	0.00	0.11	0.13	0.12	0.34	0.00	0.22	0.17	0.25	0.90	0.00
Toluene	2.14	1.20	2.11	8.37	0.36	3.01	1.95	3.20	11.73	0.68	1.40	1.43	0.78	3.01	0.33	4.75	1.43	5.94	15.22	0.81
n-Octane	0.21	0.15	0.24	1.13	0.00	0.18	0.14	0.11	0.41	0.00	0.10	0.10	0.11	0.27	0.00	0.24	0.16	0.29	0.93	0.00
Perchloroethylene	0.11	0.00	0.23	0.97	0.00	0.08	0.00	0.11	0.33	0.00	0.04	0.00	0.10	0.32	0.00	0.14	0.14	0.15	0.38	0.00
Ethylbenzene	0.29	0.19	0.24	0.86	0.00	0.41	0.24	0.40	1.33	0.13	0.26	0.25	0.19	0.61	0.00	0.95	0.34	1.08	3.22	0.19
p+m Xylene	1.47	0.44	1.76	4.38	0.10	1.16	0.50	1.36	4.26	0.36	0.50	0.54	0.38	1.41	0.00	1.80	0.40	2.49	7.18	0.18
Styrene	0.69	0.49	0.48	1.82	0.16	0.56	0.50	0.31	1.48	0.29	0.76	0.65	0.72	2.09	0.00	1.83	1.83	0.70	3.07	0.86
o-Xylene	0.31	0.20	0.32	1.10	0.00	0.45	0.21	0.47	1.48	0.14	0.20	0.23	0.14	0.46	0.00	0.73	0.23	0.92	2.75	0.11
Isopropylbenzene	0.15	0.02	0.26	1.02	0.00	0.15	0.16	0.11	0.31	0.00	0.09	0.09	0.10	0.28	0.00	0.12	0.06	0.15	0.36	0.00
a-Pinene	0.88	0.58	0.86	3.78	0.19	0.45	0.27	0.47	1.74	0.14	0.51	0.50	0.34	1.42	0.11	0.71	0.60	0.37	1.70	0.41
n-Propylbenzene	0.16	0.11	0.19	0.73	0.00	0.15	0.11	0.11	0.37	0.00	0.20	0.18	0.18	0.49	0.00	0.28	0.23	0.18	0.65	0.00
1-Ethyl-3-Methylbenzene	0.27	0.20	0.33	1.09	0.00	0.34	0.21	0.31	1.01	0.00	0.20	0.21	0.17	0.54	0.00	0.30	0.17	0.35	1.08	0.00
1-Ethyl-4-Methylbenzene	0.37	0.29	0.40	1.69	0.00	0.42	0.34	0.23	0.94	0.21	0.23	0.24	0.15	0.49	0.00	0.42	0.33	0.30	1.04	0.12
1,3,5-Trimethylbenzene	0.50	0.33	0.57	2.04	0.00	0.26	0.16	0.20	0.66	0.11	0.26	0.15	0.35	1.33	0.00	0.74	0.52	0.60	2.06	0.25
1-Ethyl-2-Methylbenzene	0.25	0.18	0.22	0.70	0.00	0.23	0.22	0.12	0.47	0.10	0.15	0.16	0.10	0.29	0.00	0.21	0.15	0.21	0.74	0.00
b-Pinene	0.82	0.75	0.62	2.38	0.00	0.59	0.51	0.48	2.02	0.13	0.75	0.60	0.65	2.08	0.00	2.06	1.70	1.00	3.74	0.94
1,2,4-Trimethylbenzene	1.11	0.49	2.10	9.21	0.12	0.54	0.36	0.48	1.57	0.14	0.85	0.81	0.48	1.75	0.17	0.77	0.59	0.53	1.50	0.12
Limonene	0.45	0.31	0.44	1.59	0.00	0.67	0.50	0.40	1.35	0.18	0.29	0.27	0.16	0.62	0.00	0.46	0.31	0.36	1.02	0.13
1,3-Diethylbenzene	0.50	0.17	0.73	2.76	0.00	0.99	0.87	0.76	2.49	0.12	0.37	0.31	0.17	0.68	0.18	0.34	0.26	0.23	0.78	0.13
n-Butylbenzene	0.30	0.20	0.37	1.57	0.00	0.31	0.25	0.17	0.62	0.00	0.18	0.19	0.14	0.41	0.00	0.27	0.26	0.12	0.49	0.14
Sampling days used for seasonal averages	9/26/1992	9/16/1993	12/2/1992	2/18/1993	3/2/1993	5/31/1993	6/6/1993	6/12/1993	6/18/1993	6/24/1993	7/18/1993	7/24/1993	7/30/1993	8/5/1993	8/11/1993	8/23/1993	5/25/1993			
	10/2/1992	9/22/1993	12/14/1992	3/8/1993	3/20/1993	4/1/1993	4/7/1993	4/13/1993	4/25/1993	5/1/1993	5/7/1993	5/13/1993	5/21/1993	5/26/1993	5/31/1993	6/1/1993	6/11/1993	6/17/1993		
	10/9/1992	9/28/1993	12/20/1992	3/10/1993	3/26/1993	4/17/1993	5/1/1993	5/13/1993	5/21/1993	5/28/1993	6/4/1993	6/11/1993	6/18/1993	6/25/1993	7/2/1993	7/9/1993	7/16/1993	7/23/1993		
	10/15/1992	10/4/1993	12/26/1992	1/1/1993	1/18/1993	1/25/1993	1/11/1993	1/18/1993	1/25/1993	1/31/1993	1/20/1993	1/27/1993	1/34/1993	1/21/1993	1/28/1993	2/4/1993	2/11/1993	2/18/1993		
	10/21/1992	10/10/1993	1/27/1992	1/7/1993	1/14/1993	1/21/1993	1/11/1993	1/18/1993	1/25/1993	1/31/1993	1/20/1993	1/27/1993	1/34/1993	1/21/1993	1/28/1993	2/4/1993	2/11/1993	2/18/1993		
	11/2/1992	11/8/1992	11/14/1992	11/20/1992	11/26/1992	11/10/1993	11/17/1993	11/23/1993	11/30/1993	12/7/1993	12/14/1993	12/21/1993	12/28/1993	1/4/1994	1/11/1994	1/18/1994	1/25/1994	1/32/1994		
	11/10/1993	11/16/1993	11/23/1993	11/30/1993	12/7/1993	12/14/1993	12/21/1993	12/28/1993	1/4/1994	1/11/1994	1/18/1994	1/25/1994	1/32/1994	2/8/1994	2/15/1994	2/22/1994	2/29/1994	3/6/1994		

Table 1d. Seasonal averages of hydrocarbon compound concentrations in ppbC at Candor, North Carolina

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min
Ethene	1.67	1.25	1.06	3.87	0.77	2.28	2.30	1.17	4.64	0.72	1.93	1.18	1.83	6.37	0.00	0.47	0.31	0.55	1.43	0.00
Acetylene	1.34	0.92	1.07	3.84	0.37	2.53	2.56	0.86	4.55	1.37	1.12	0.64	1.34	3.85	0.00	0.17	0.00	0.42	1.03	0.00
Ethane	2.51	1.84	2.42	8.08	0.00	2.81	2.46	1.73	6.66	0.00	1.67	1.59	1.90	5.67	0.00	0.09	0.00	0.21	0.52	0.00
Propene	0.70	0.77	0.34	1.31	0.11	0.78	0.74	0.30	1.39	0.40	0.41	0.29	1.20	0.18	1.75	1.76	1.47	3.29	0.27	
Propane	3.77	1.87	4.36	15.63	0.43	5.84	5.16	3.23	12.70	0.61	3.44	3.19	2.69	10.82	0.00	2.19	2.20	0.59	3.04	1.37
Isobutane	0.97	0.64	0.99	3.61	0.10	1.71	1.74	0.85	3.78	0.71	0.83	0.76	0.61	2.20	0.00	0.45	0.40	0.18	0.73	0.26
Isobutene + 1-Butene	1.24	0.85	1.13	4.54	0.43	0.48	0.50	0.28	0.80	0.00	0.66	0.57	0.70	2.67	0.00	0.96	0.68	0.87	2.61	0.29
n-Butane	2.83	1.81	2.63	9.74	0.52	4.97	4.86	2.97	13.11	1.74	2.15	1.76	1.58	5.41	0.00	0.98	1.04	0.34	1.38	0.43
Trans-2-butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.54	1.76	0.00	1.43	0.00	3.51	8.59	0.00
Cis-2-butene	0.01	0.00	0.05	0.16	0.00	0.01	0.00	0.03	0.11	0.00	0.18	0.00	0.38	1.31	0.00	0.00	0.00	0.00	0.00	0.00
3-methyl-1-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopentane	2.91	2.52	1.50	5.94	1.12	2.65	2.67	1.50	6.33	0.86	2.08	1.52	1.57	5.66	0.33	3.13	1.96	2.91	8.70	0.83
1-Pentene	0.10	0.00	0.27	0.93	0.00	0.35	0.15	0.41	1.13	0.00	0.32	0.20	0.37	1.53	0.00	0.14	0.07	0.21	0.54	0.00
2-methyl-1-Butene	0.03	0.00	0.06	0.18	0.00	0.02	0.00	0.06	0.17	0.00	0.04	0.00	0.06	0.14	0.00	0.02	0.00	0.05	0.13	0.00
n-Pentane	1.17	0.60	1.14	3.30	0.22	1.55	1.47	0.84	3.50	0.62	1.04	0.89	0.70	2.32	0.29	1.00	0.76	0.67	2.24	0.41
Isoprene	2.45	0.55	3.62	9.23	0.00	0.01	0.00	0.03	0.10	0.00	1.84	0.44	2.97	10.99	0.00	10.02	6.70	9.96	27.54	1.40
Trans-2-pentene	0.03	0.00	0.07	0.23	0.00	0.05	0.00	0.10	0.35	0.00	0.07	0.00	0.11	0.34	0.00	0.02	0.00	0.05	0.12	0.00
Cis-2-pentene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-methyl-2-Butene	0.14	0.14	0.03	0.18	0.09	0.07	0.00	0.15	0.41	0.00	0.05	0.00	0.07	0.16	0.00	0.87	0.84	0.81	2.01	0.00
3-methyl-1-Pentene	0.19	0.16	0.16	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.18	0.46	1.24	0.00	0.32	0.17	0.38	0.88	0.00
4-methyl-1-Pentene	0.04	0.00	0.11	0.34	0.00	0.17	0.19	0.09	0.29	0.00	0.16	0.15	0.10	0.31	0.00	0.02	0.00	0.05	0.13	0.00
Cyclopentane	0.15	0.14	0.08	0.30	0.00	0.19	0.18	0.06	0.35	0.11	0.11	0.13	0.09	0.28	0.00	0.07	0.00	0.12	0.29	0.00
2-Methylpentane	0.81	0.75	0.54	1.77	0.16	0.88	0.80	0.48	1.85	0.24	1.22	1.11	1.01	3.98	0.22	2.81	2.43	1.62	5.44	1.17
3-Methylpentane	0.57	0.49	0.42	1.30	0.11	0.86	0.85	0.37	1.37	0.23	0.69	0.55	0.41	1.52	0.20	0.39	0.48	0.21	0.54	0.00
n-Hexane	0.73	0.38	0.69	1.97	0.13	0.73	0.63	0.43	1.57	0.24	0.56	0.39	0.43	1.53	0.15	0.28	0.27	0.19	0.57	0.00
Cis-3-hexene	0.13	0.16	0.10	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.05	0.15	0.53	0.00	0.22	0.07	0.29	0.63	0.00
Methylcyclopentane	0.22	0.18	0.23	0.73	0.00	0.33	0.34	0.17	0.74	0.13	0.19	0.16	0.16	0.48	0.00	0.19	0.16	0.20	0.52	0.00
2,4-Dimethylpentane	0.13	0.13	0.11	0.34	0.00	0.13	0.14	0.10	0.32	0.00	0.13	0.13	0.12	0.37	0.00	0.13	0.08	0.17	0.44	0.00
2,3-Dimethylpentane	0.40	0.36	0.16	0.68	0.13	0.32	0.30	0.14	0.53	0.00	0.59	0.41	0.54	2.09	0.00	0.75	0.67	0.29	1.31	0.53
1,1,1-Trichloroethane	0.21	0.16	0.11	0.44	0.11	0.30	0.28	0.16	0.65	0.10	0.22	0.18	0.12	0.47	0.10	0.36	0.36	0.11	0.50	0.23
Benzene	12.77	12.86	8.35	24.67	2.14	1.59	1.47	0.53	2.73	0.97	1.00	0.87	0.40	1.83	0.45	0.90	0.85	0.36	1.52	0.58
Cyclohexane	0.05	0.00	0.09	0.26	0.00	0.26	0.12	0.39	1.35	0.00	0.11	0.12	0.11	0.32	0.00	0.02	0.00	0.05	0.12	0.00
2,3-Dimethylhexane	0.28	0.17	0.68	0.10	0.26	0.12	0.53	0.14	0.29	0.23	0.34	0.34	1.42	0.00	0.41	0.27	0.25	0.74	0.21	

Table 1d. Seasonal averages of hydrocarbon compound concentrations in ppbC at Candor, North Carolina

Compound	Autumn					Winter					Spring					Summer				
	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min	Mean	Medn	Std	Max	Min
2,3,4-Trimethylpentane	0.18	0.14	0.11	0.37	0.00	0.12	0.13	0.11	0.31	0.00	0.10	0.11	0.10	0.30	0.00	0.13	0.00	0.21	0.43	0.00
Toluene	2.26	1.79	1.22	5.33	1.31	1.83	1.83	0.91	3.49	0.63	1.43	1.25	0.86	3.26	0.44	2.94	2.53	1.97	6.31	1.20
n-Octane	0.37	0.20	0.37	1.29	0.12	0.16	0.12	0.16	0.61	0.00	0.17	0.13	0.21	0.73	0.00	0.49	0.47	0.48	1.12	0.00
Perchloroethylene	0.08	0.00	0.25	0.88	0.00	0.02	0.00	0.05	0.18	0.00	0.05	0.00	0.07	0.18	0.00	0.56	0.00	0.98	2.39	0.00
Ethylbenzene	0.31	0.30	0.13	0.66	0.19	0.29	0.13	0.47	0.00	0.20	0.20	0.16	0.49	0.00	0.48	0.48	0.30	1.02	0.19	
m+p Xylene	0.77	0.62	0.42	1.81	0.42	0.67	0.62	0.30	1.13	0.12	0.47	0.37	0.37	1.35	0.00	1.63	1.75	1.31	3.38	0.12
Styrene	0.81	0.82	0.21	1.16	0.41	0.47	0.52	0.18	0.79	0.14	0.98	1.15	0.74	2.28	0.00	2.75	2.32	1.28	5.09	1.81
o-Xylene	0.30	0.25	0.15	0.75	0.19	0.27	0.27	0.12	0.48	0.00	0.17	0.13	0.17	0.56	0.00	0.81	0.67	0.86	2.36	0.00
Isopropylbenzene	0.15	0.15	0.10	0.36	0.00	0.09	0.10	0.10	0.24	0.00	0.10	0.00	0.15	0.56	0.00	0.56	0.51	0.59	1.40	0.00
a-Pinene	1.31	0.95	0.92	3.53	0.41	0.71	0.40	0.67	2.48	0.10	0.73	0.75	0.46	1.73	0.13	2.25	2.31	0.86	3.22	0.71
n-Propylbenzene	0.16	0.16	0.07	0.27	0.00	0.09	0.11	0.07	0.19	0.00	0.21	0.14	0.17	0.54	0.00	0.94	0.54	1.17	3.22	0.14
1-ethyl-3-Methylbenzene	0.26	0.24	0.13	0.60	0.13	0.20	0.21	0.10	0.36	0.00	0.11	0.00	0.17	0.51	0.00	1.21	0.82	1.50	3.99	0.00
1-ethyl-4-Methylbenzene	0.45	0.40	0.16	0.87	0.30	0.36	0.32	0.11	0.56	0.22	0.26	0.25	0.13	0.51	0.00	1.30	0.99	1.18	3.33	0.34
1,3,5-Trimethylbenzene	0.23	0.27	0.11	0.42	0.00	0.16	0.14	0.07	0.38	0.09	0.13	0.11	0.12	0.37	0.00	0.56	0.28	0.73	1.78	0.00
1-ethyl-2-Methylbenzene	0.21	0.22	0.09	0.41	0.10	0.21	0.20	0.09	0.36	0.10	0.18	0.20	0.11	0.33	0.00	1.01	0.99	1.00	2.56	0.00
b-Pinene	0.97	0.80	0.66	2.24	0.17	0.68	0.67	0.38	1.51	0.21	0.69	0.67	0.45	1.60	0.00	1.30	1.29	0.39	1.88	0.89
1,2,4-Trimethylbenzene	0.39	0.37	0.13	0.68	0.19	0.53	0.36	0.48	1.99	0.19	6.26	5.10	5.98	17.04	0.35	6.79	8.30	4.66	12.29	1.11
Limonene	0.47	0.44	0.23	0.87	0.18	0.50	0.37	0.24	1.02	0.22	0.33	0.29	0.35	1.47	0.00	0.69	0.60	0.53	1.32	0.12
1,3-Diethylbenzene	0.44	0.25	0.41	1.24	0.10	0.86	0.95	0.55	1.78	0.10	0.42	0.31	0.39	1.56	0.00	0.84	0.85	0.71	1.77	0.11
n-Butylbenzene	0.26	0.24	0.11	0.49	0.14	0.30	0.31	0.14	0.62	0.00	0.21	0.19	0.20	0.76	0.00	1.49	1.42	1.47	3.58	0.00
Sampling days used for seasonal averages	9/3/1992	9/9/1992	9/27/1992	10/3/1992	10/15/1992	10/21/1992	11/1/1992	11/14/1992	11/17/1992	11/20/1992	11/26/1992	11/8/1992	11/13/1992	11/19/1992	11/25/1992	12/2/1992	12/8/1992	12/14/1992	12/20/1992	12/26/1992
	9/13/1993	5/19/1993	5/25/1993	5/31/1993	6/1/1993	6/14/1993	6/20/1993	6/26/1993	6/30/1993	7/6/1993	7/12/1993	7/18/1993	7/24/1993	7/30/1993	8/6/1993	8/12/1993	8/18/1993	8/24/1993	8/30/1993	9/5/1993

This seasonal variation of the paraffins and acetylene is consistent with the literature. A study by Jobson et al., [1994] found that at a remote boreal site in Canada, alkane compounds and acetylene concentrations displayed a winter maximum and summer minimum; Penkett et al., [1993] observed seasonal trends in hydrocarbon concentrations in air over the North Atlantic Ocean. Seasonal variations of atmospheric hydrocarbons were also measured in western France [Boudries et al. 1994] and at a rural site in Norway [Hov et al. 1991]. The winter maximum and summer minimum of the lower alkanes and acetylene has been attributed to hydroxyl chemistry and the seasonal abundance of the OH radical [Jobson et al. 1994, Penkett et al. 1993, Boudries et al. 1994, Lightman et al. 1990, Spivakovsky et al. 1990]. The seasonal variation in hydrocarbon source strengths, and differences in atmospheric behavior such as increased convection and vertical mixing in the summer, or differences in air mass climatology with season, also play a role in the hydrocarbon seasonal variation [Jobson et.al 1994].

The sum of C₂-C₁₀ hydrocarbons (Figure 3) did not vary greatly between the autumn, winter and spring, ranging from approximately 30 to 50 ppbC for these three seasons. However, the summer period shows much higher concentrations, accounted for primarily by increased concentrations of the biogenic sums.

The paraffin sum displays a seasonal pattern with a winter maximum for all but the Oak Grove site, which displays its maximum during the summer. This can be attributed to n-pentane (16.51 ± 20.97 ppbC, median = 7.68 ppbC), which is almost 8 times greater than the second highest value, 2.15 ± 2.28 ppbC at the Yorkville site, as shown in Figure 4. During the summer, Oak Grove had some unusually large values of n-pentane. Out of 12 observations, 2 days had values of ~ 57 ppbC, one day measured 29 ppbC and two days measured approximately 15 ppbC. The reason for these high n-pentane values are uncertain; however, auto emissions is ruled out as a possible source because of the low acetylene values.

The olefins sum, which does not include the biogenic hydrocarbons isoprene, α -pinene, β -pinene and limonene, shows little variation throughout the year, ranging between ~ 4 and 7 ppbC among the sites. During the summer, however, olefin concentrations at Yorkville are higher than the other three sites (10.72 ppbC). Studies

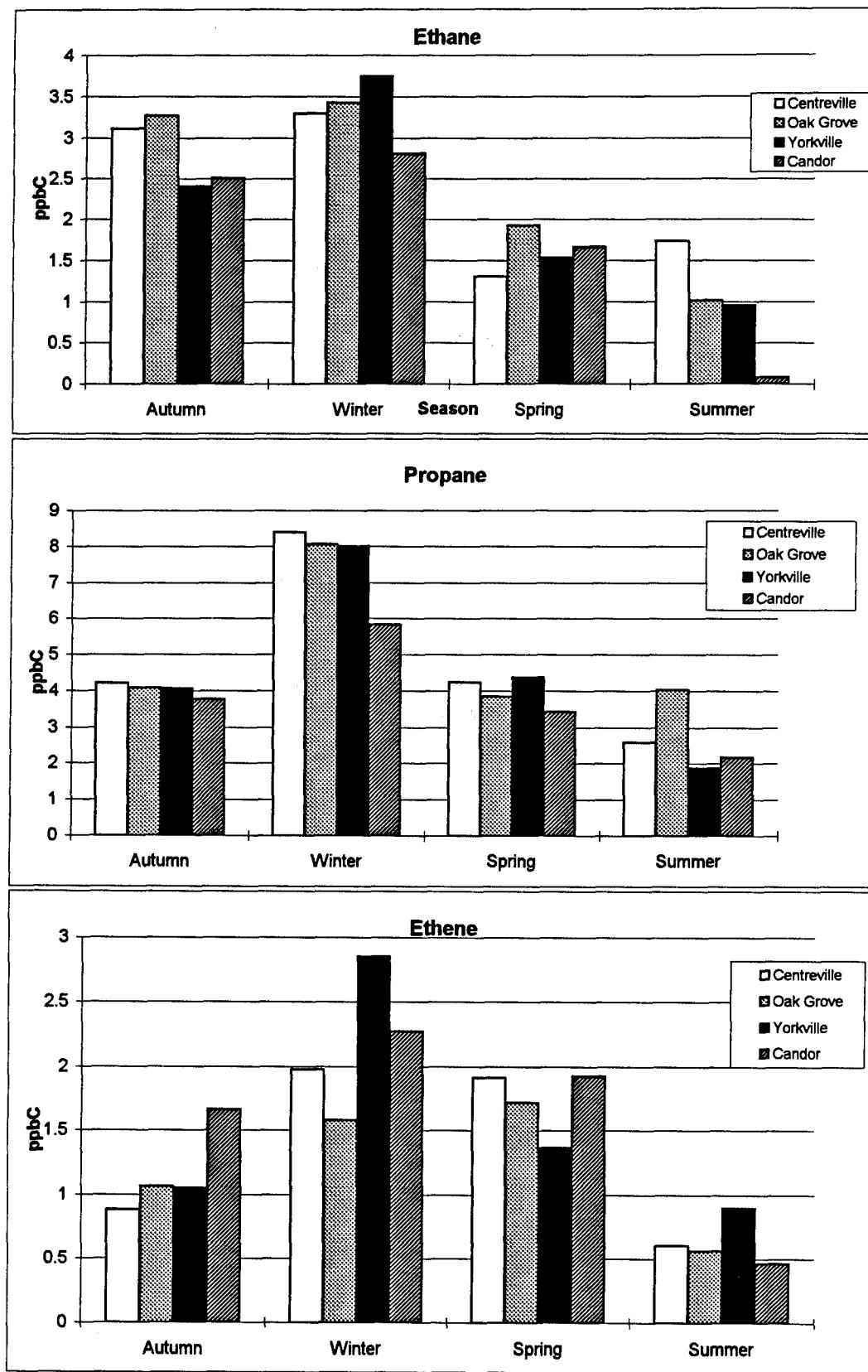


Figure 2. Seasonal averages of select C₂-C₄ hydrocarbons

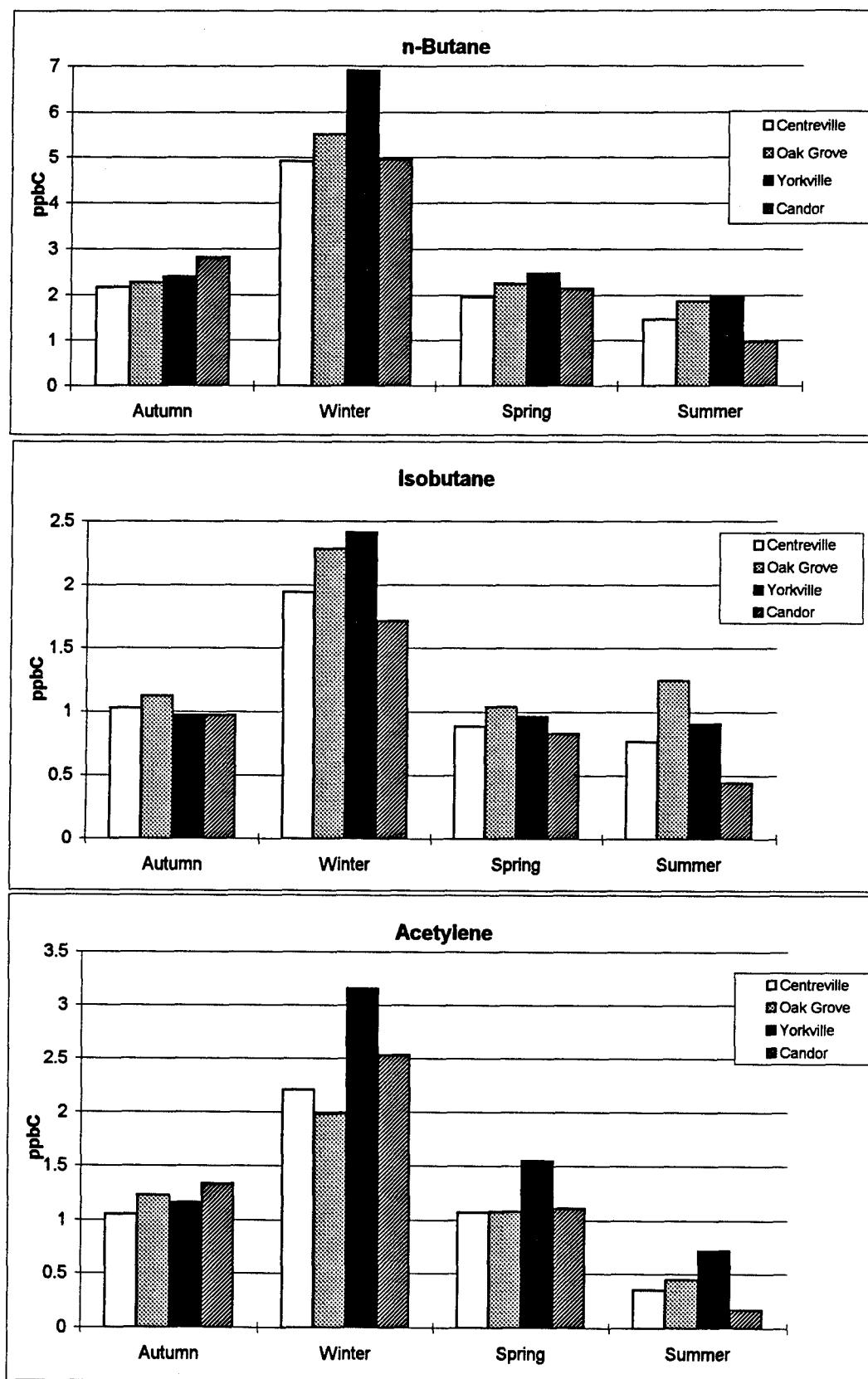


Figure 2 continued. Seasonal averages of select C₂-C₄ hydrocarbons

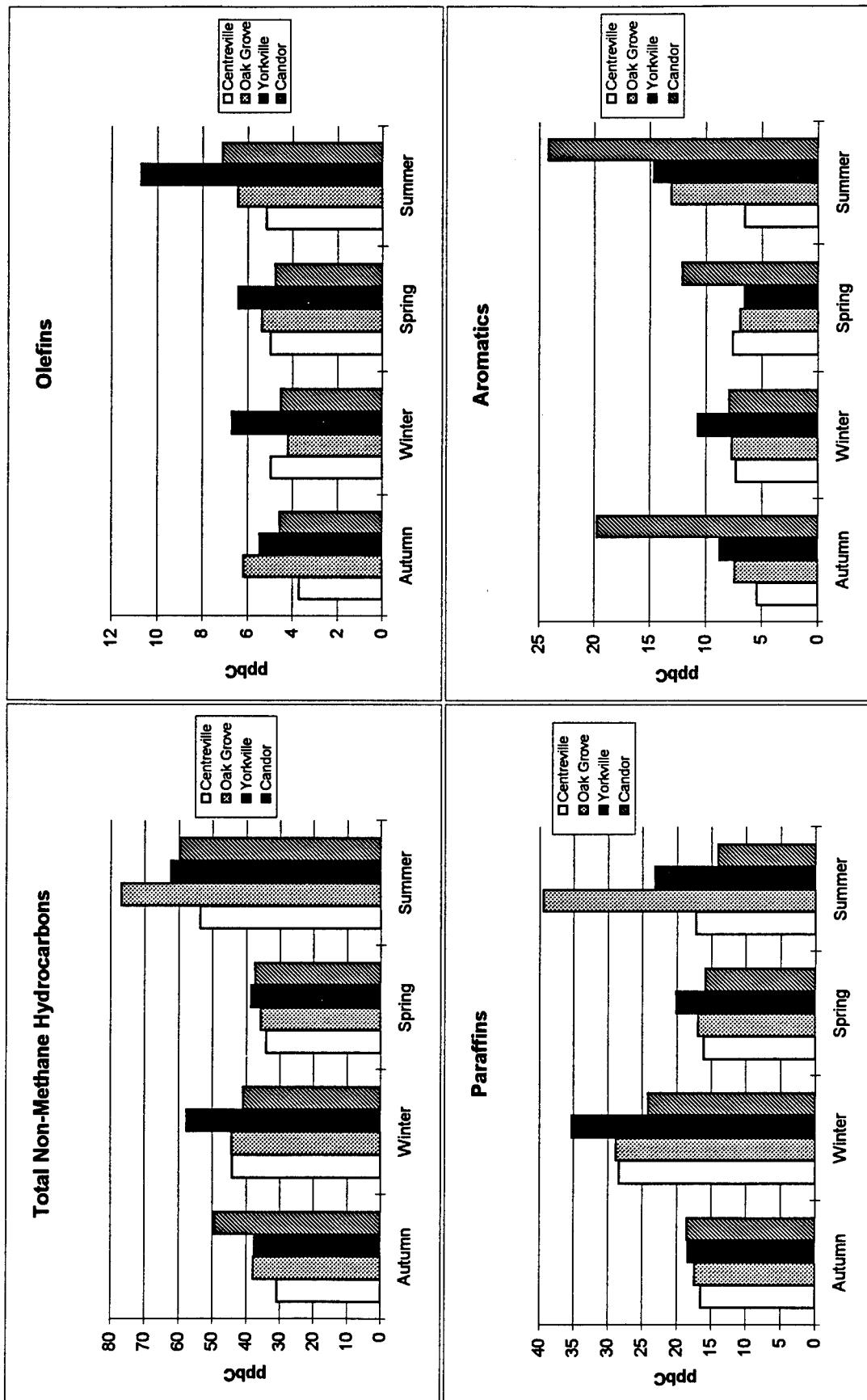


Figure 3. Seasonal averages of hydrocarbon sums (olefins do not include isoprene, α -, β -pinene, and limonene)

have shown that there is no distinct seasonal trend for olefins at continental remote sites unaffected by anthropogenic sources [Jobson et al., 1994], and very little seasonal variation in the free troposphere over the Atlantic [Penkett et al., 1993]. Hov et al [1991] found a seasonal trend for ethene and propene with a late January maxima and a secondary maxima during July-August, but attributed this summer maxima to local release from areas upwind of the site. Yorkville is affected by two potential emission sources; the city of Atlanta, located approximately 45 miles (72 km) southeast of the Yorkville site, and a large power generating station located approximately 30 miles (48 km) east of Yorkville [Kirk 1996]. The summer maxima for the olefins at Yorkville may be due to transport from these anthropogenic emission sources.

While Oak Grove and Yorkville display summer aromatic concentrations approximately two times higher than during the other three seasons, the Candor site displays extraordinarily large concentrations of the aromatic sums during both the autumn and summer seasons. The difference between the high aromatic concentration during autumn at Candor (19.75 ppbC) and the other three sites (~ 5-8 ppbC) is accounted for by benzene (12.77 ± 8.35 ppbC). The difference between the high summer aromatic sum at Candor and the Yorkville site is due primarily to 1,2,4-trimethylbenzene (6.79 ± 4.66), along with the compounds styrene (2.75 ± 1.28) and toluene (2.94 ± 1.97). Figure 4 shows the compounds n-pentane, benzene, and 1,2,4-trimethylbenzene, which exhibit particularly high concentrations. The reason for the high levels of these particular compounds is unclear. Surface wind direction appears to have a random relationship with excessively high concentrations of n-pentane, benzene, and 1,2,4-trimethylbenzene.

Table 2 summarizes selected hydrocarbons measured during the summer at various rural and remote sites. It can be seen that hydrocarbon concentrations at the Centreville site are comparable to the rural Norway and Maine sites listed in Table 2. The Fraserdale site in Canada appears to be the least affected by anthropogenic sources, given its lower concentrations of acetylene and the other lower molecular weight hydrocarbons.

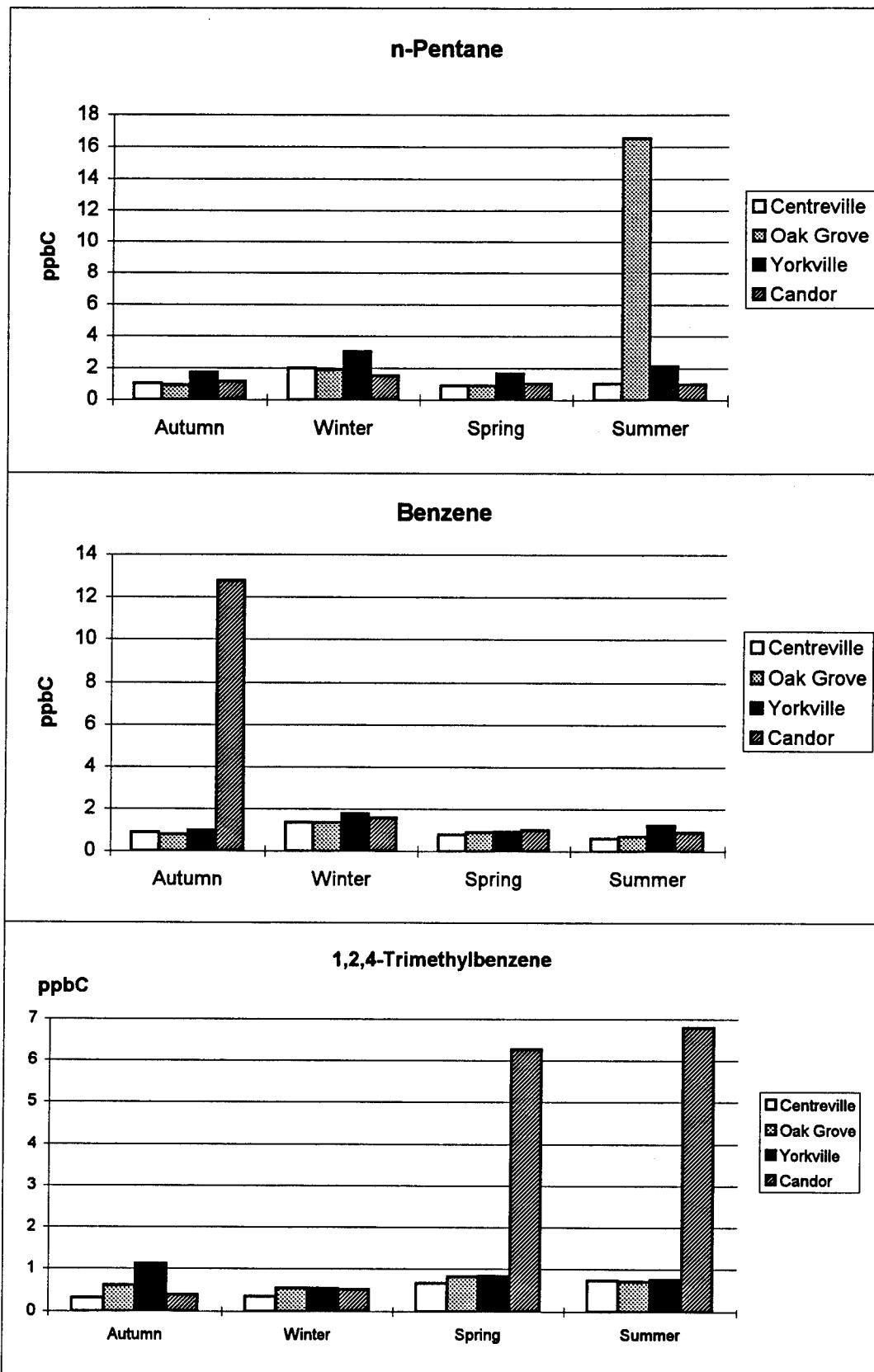


Figure 4. Hydrocarbons with abnormally high values

Table 2. Average hydrocarbon concentrations (ppbC) at various rural sites during the summer months

Compound	Fraserdale Canada ¹	Birkenes Norway ²	Belfast Maine ³	NW ⁴ England	Centreville Alabama ⁵	Raleigh NC ⁶	Brazil ⁷
Ethene		1.67	2.0	1.6	0.61		3.78
Acetylene	0.15	0.51	<0.5	0.6	0.36		
Ethane	1.64	3.05	3.5*	14.9	1.74		4.18
Propene		0.82	0.5	4.1	0.73	0.54	.93
Propane	0.23	2.01	2.0	10.3	2.60	9.59	1.35
Isobutane	0.028	0.70	0.5	0.8	0.77	0.61	
n-Butane	0.06	1.67	2.0	1.1	1.48	2.04	0.96
Isopentane	0.04	1.00	1.0		2.22	4.42	
n-Pentane	0.065	0.62	1.0	5.1	1.04	1.97	<DL
2-Methylpentane				<0.5	3.34	1.28	
3-Methylpentane				<0.5	0.82	0.70	
n-Hexane				5.1	0.68	0.87	<DL
Cis-3-hexene				<0.5	0.70		
Benzene					0.61	1.32	3
Toluene					1.20	8.96	0.84

* Geometric mean

Reference	Sampling Period
1 Jobson et al., 1994	July to September 1990, 1991 and 1992, collected midmorning (0900 to 1200). Samples from June to July 1990 were collected throughout the day.
2 Hov et al., 1991	June-August 1987
3 Sexton and Westberg, 1984	June-July 1975
4 Colbeck and Harrison, 1985	May-July 1983
5 This study	June-August 1993, 1200-1300 local time
6 Lawrimore et al., 1995 (semi-urban)	surface, August 1993, 0500-0800 EDT
7 Greenberg and Zimmerman, 1984.	surface, August and September 1979 and 1980

Table 3. Summer averages of biogenic hydrocarbons (ppbC)

Location	Isoprene	a-Pinene	b-Pinene	Limonene
Raleigh, NC ¹	2.08			
Brazil ²	12	2.7		
Niwot Ridge, CO ³	3.15	1.4	0.7	
Candor, North Carolina ⁴	10.01	2.25	1.30	0.69
Centreville, Alabama ⁵	21.15	1.60	1.36	0.24
Oak Grove, Mississippi ⁵	11.19	2.71	3.04	0.63
Yorkville, Georgia ⁵	9.8	0.71	2.06	0.46

1 Lawrimore et al., 1995 (surface, August 1993, 0500-0800 EDT)

2 Greenberg and Zimmerman, 1984 (surface, August and September 1979 and 1980)

3 Greenberg and Zimmerman, 1984 (surface, August-September and November 1982)

4 This work (June 1992 and 1993, 1200-1300 local time)

5 This work (June-August 1993 1200-1300 local time)

3.2. Biogenic Hydrocarbons

Isoprene averaged approximately 2 ppbC during the autumn and spring, and was virtually nonexistent during the winter period for all four sites (mean < 0.1 ppbC) (Figure 5a). Isoprene concentrations were highest during the summer, with Centreville having concentrations twice as high as the other three sites. The terpenes, which include the naturally emitted compounds α -pinene, β -pinene and limonene, also show a seasonal distribution with lowest concentrations in the winter and highest in the summer (Figure 5b). However, unlike isoprene, terpenes are emitted throughout the winter, the sum ranging between 1.25 and 1.9 ppbC for all sites. A study done by Tingey [1981] on live oak found that isoprene was emitted only in daylight, and given constant light conditions, the emission rate is temperature dependent. While isoprene is highly dependent on temperature and virtually negligible during the winter, the terpenes have a small winter abundance. Terpene emissions from slash pine do not vary with light, but emission rates are log-linearly related to temperature [Tingey 1981]. Table 3 lists isoprene and monoterpene data from this work and other literature.

Figure 6 shows the linear relationship between the logarithm of isoprene (ppbC) and temperature ($^{\circ}$ C) using data collected from all four sites. The plot includes all values for which isoprene was greater or equal to 1 ppbC (April through September). The regression equation is

$$\log(\text{isoprene}) = -0.67944 + 0.056202T$$

with an R-squared value of 0.53. The units of isoprene are in ppbC. The slope of the best fit line (0.056) is lower than that found by Jobson et al. [1994], who found a slope of 0.071. The regression equation found by Jobson in units of ppbv was

$$\log(\text{isoprene}) = -1.40 + 0.071T \quad (\text{in units of ppbv})$$

$$\log(\text{isoprene}) = -0.70103 + 0.071T \quad (\text{converted to units of ppbC})$$

Converting this equation for units of ppbC changes only the intercept to a value of

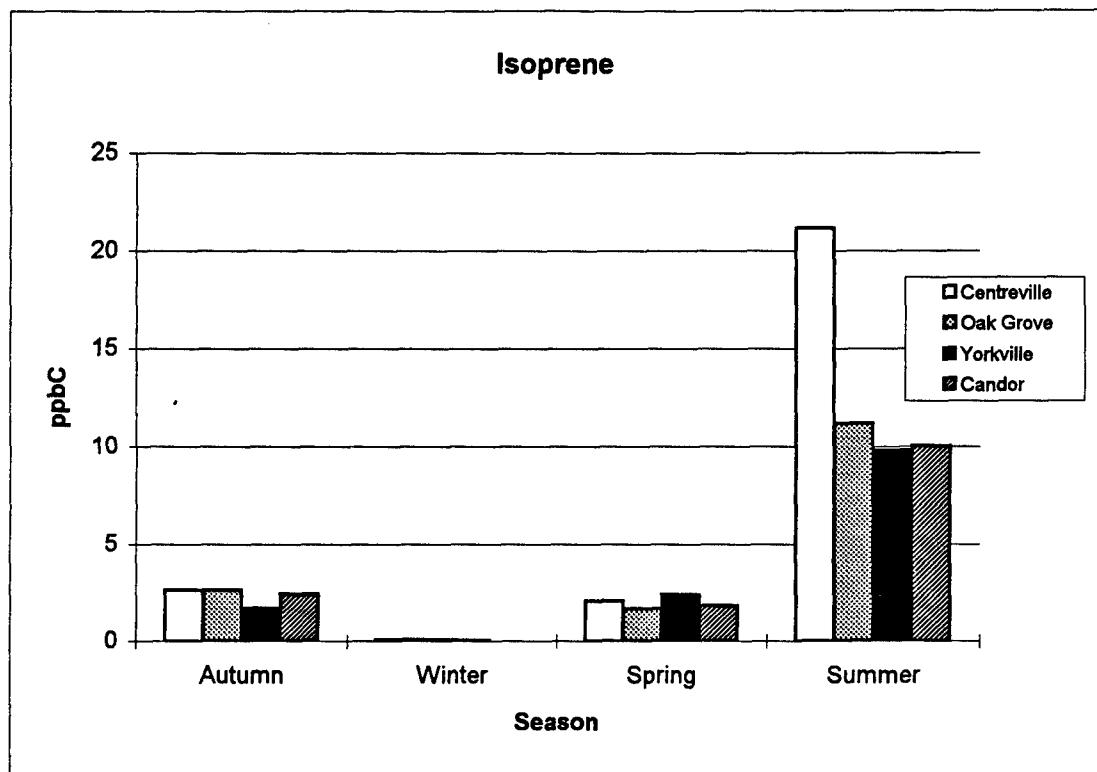


Figure 5a. Seasonal average of isoprene

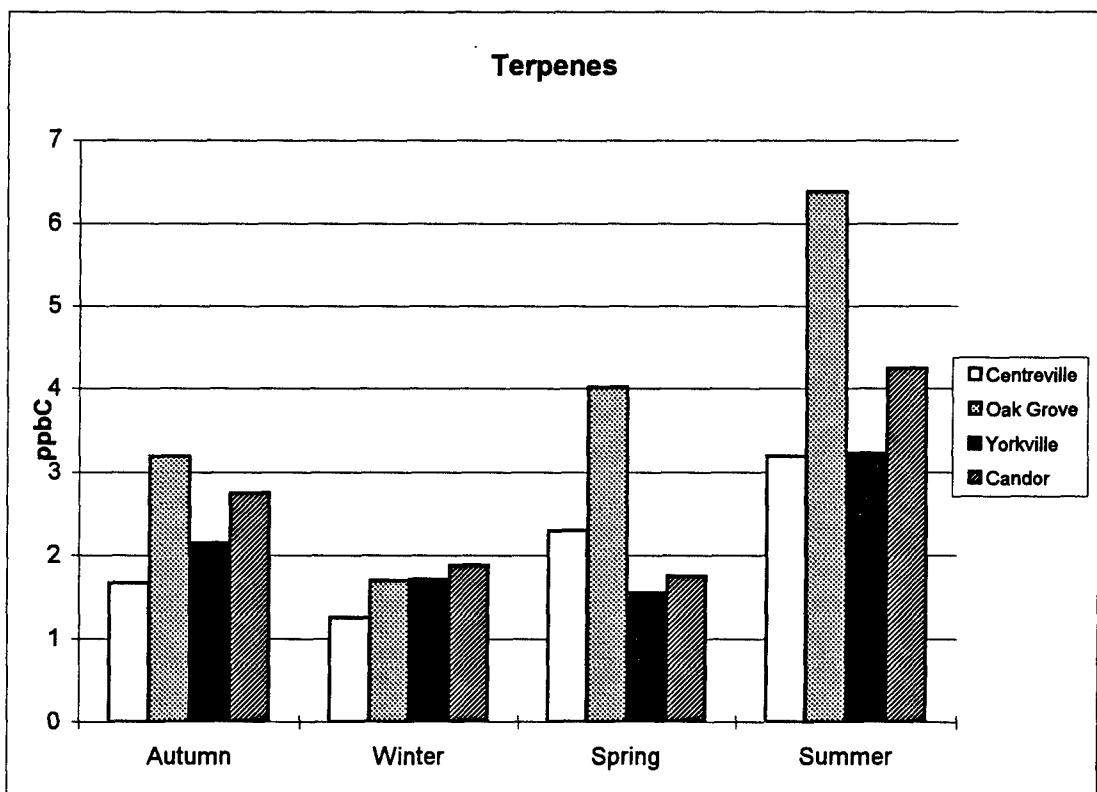


Figure 5b. Seasonal average of terpene sum (α -, β -pinene, limonene)

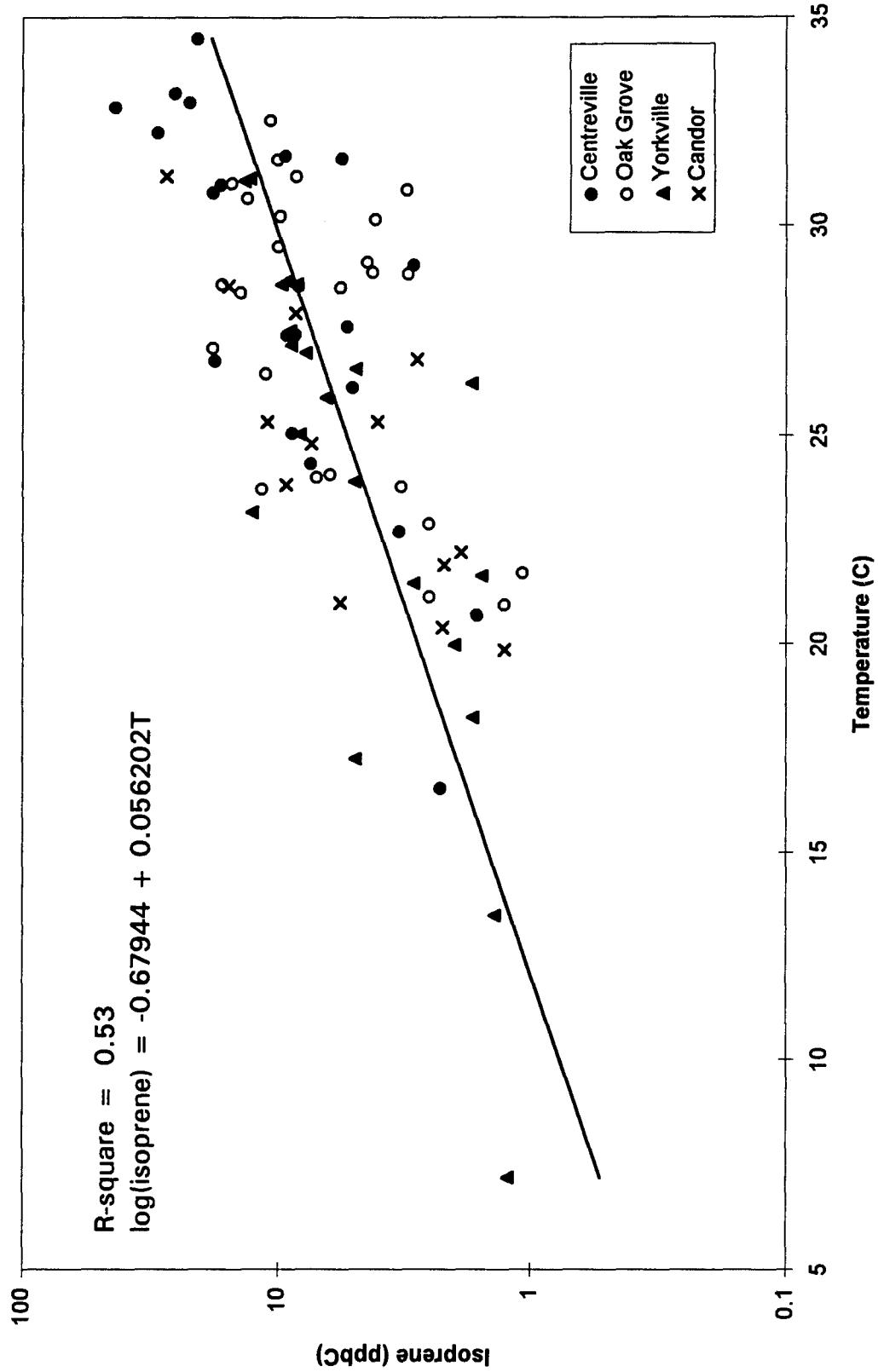


Figure 6. Isoprene concentration versus temperature for the months April through September 1992 and 1993.

-0.70103 and the slope remains the same. Considering a temperature range of 18° to 35°C, the predicted isoprene concentrations using Jobson's regression equation was two to three times greater than the predicted concentrations using the regression equation found in this work (refer to Table 4). Part of this discrepancy may be due to the fact that in this work, four sites were used for the regression, versus Jobson's one site, which increases the variability of isoprene concentrations. To account for this difference, a regression of isoprene at only one site, Centreville, resulted in a higher R-squared value (0.61) and a slope very similar to Jobson (0.066), but with a lower intercept. The regression equation for Centreville turned out to be

$$\log(\text{isoprene}) = -0.9029 + 0.066T$$

Another reason which may explain the difference in regression equation terms is that the relationship between isoprene and temperature is affected by the type of surrounding vegetation, as well the atmospheric concentration of OH and ozone. Other possible factors which can influence measured isoprene concentrations include the time of day when samples were collected, and atmospheric conditions, such as the height of the boundary layer or vertical mixing and turbulence in the atmosphere. Table 5 lists the correlation coefficients between meteorological parameters and biogenically emitted hydrocarbons. The data for the correlations include sampling days from all four seasons. Isoprene is much more dependent on temperature than it is on solar radiation. The correlation coefficient between temperature and isoprene ranges between 0.62 (Candor) to 0.76 (Yorkville). The correlation between isoprene and solar radiation is less than 0.3 for all sites.

Table 4. Comparison of predicted isoprene values using regression equations from Jobson [1994], the regression of all sites, and the regression equation from only Centreville.

T (°C)	Predicted Isoprene (ppbC)			Ratios	
	Jobson	All sites	Centreville	Jobson/all	Cnvt/all
18.00	3.78	2.15	1.93	1.76	0.90
20.00	5.24	2.78	2.61	1.88	0.94
21.00	6.17	3.17	3.04	1.95	0.96
22.00	7.26	3.61	3.54	2.01	0.98
23.00	8.55	4.10	4.12	2.08	1.00
24.00	10.07	4.67	4.80	2.16	1.03
25.00	11.86	5.32	5.59	2.23	1.05
26.00	13.96	6.05	6.50	2.31	1.07
27.00	16.44	6.89	7.57	2.39	1.10
28.00	19.36	7.84	8.81	2.47	1.12
29.00	22.80	8.92	10.26	2.56	1.15
30.00	26.85	10.15	11.94	2.64	1.18
31.00	31.62	11.56	13.90	2.74	1.20
32.00	37.24	13.15	16.18	2.83	1.23
33.00	43.85	14.97	18.84	2.93	1.26
34.00	51.64	17.04	21.93	3.03	1.29
35.00	60.81	19.39	25.53	3.14	1.32

Regression equations in units of ppbC:

$$\text{Jobson et al., 1994: } \log(\text{isoprene}) = -0.70103 + 0.071T$$

$$\text{This work, all sites: } \log(\text{isoprene}) = -0.67944 + 0.056202T$$

$$\text{This work, Centreville: } \log(\text{isoprene}) = -0.9029 + 0.066T$$

Table 5. Correlation coefficients between biogenically emitted hydrocarbons and meteorological variables. The values in boldface indicate correlations >0.5 or <-0.5.

Centreville	Temp	Relhum	pBARO	Solar	Max O3	Isoprene	α -Pinene	β -Pinene	Limonene
TEMP	1.00								
RELHUM	0.03	1.00							
pBARO	-0.25	-0.49	1.00						
SOLRAD	0.32	-0.65	0.21	1.00					
OzoneMax	0.51	-0.35	-0.07	0.48	1.00				
Isoprene	0.70	0.02	-0.07	0.16	0.11	1.00			
α -Pinene	0.55	0.32	-0.23	-0.13	-0.05	0.76	1.00		
β -Pinene	0.34	0.14	-0.35	0.01	0.10	0.33	0.39	1.00	
Limonene	-0.32	0.26	-0.10	-0.12	-0.16	-0.27	-0.16	-0.04	1.00

Oak Grove	TEMP	Relhum	pBARO	SOLRAD	Max O3	Isoprene	α -Pinene	β -Pinene	Limonene
TEMP	1.00								
RELHUM	0.04	1.00							
pBARO	-0.39	-0.29	1.00						
SOLRAD	0.38	-0.79	0.08	1.00					
Max Ozone	0.44	-0.47	-0.13	0.61	1.00				
Isoprene	0.67	0.17	-0.15	0.13	0.12	1.00			
α -Pinene	0.45	0.31	-0.34	-0.01	0.08	0.63	1.00		
β -Pinene	0.57	0.28	-0.23	0.06	0.21	0.50	0.65	1.00	
Limonene	0.02	0.22	-0.03	-0.16	-0.21	0.02	0.00	0.07	1

Yorkville	TEMP	Relhum	pBARO	SOLRAD	Max O3	Isoprene	α -Pinene	β -Pinene	Limonene
TEMP	1.00								
RELHUM	-0.07	1.00							
pBARO	-0.12	-0.30	1.00						
SOLRAD	0.33	-0.65	0.26	1.00					
max ozone	0.81	-0.26	-0.06	0.41	1.00				
Isoprene	0.76	0.00	0.06	0.18	0.63	1.00			
α -Pinene	0.17	0.49	-0.23	-0.54	-0.06	0.17	1.00		
β -Pinene	0.60	0.31	-0.11	-0.05	0.55	0.59	0.38	1.00	
Limonene	-0.19	0.23	0.12	-0.39	-0.21	-0.09	0.40	0.12	1

Candor	TEMP	Relhum	Max O3	Solar	Isoprene	α -Pinene	β -Pinene	Limonene
TEMP	1.00							
RELHUM	-0.04	1.00						
max ozone	0.63	-0.51	1.00					
SOLRAD	0.31	-0.71	0.62	1.00				
Isoprene	0.62	-0.02	0.43	0.25	1.00			
Benzene	0.38	0.25	0.00	-0.07	0.16			
α -Pinene	0.43	0.53	-0.03	-0.26	0.34	1.00		
β -Pinene	0.31	0.55	-0.02	-0.45	0.10	0.70	1.00	
Limonene	-0.34	0.28	-0.37	-0.39	-0.03	0.36	0.30	1.00

3.3. Effect of Hydrocarbon Reactivity with Hydroxyl Radical

Characterizing the abundance of hydrocarbons at a site provides information concerning source contribution, however, it does not take into account individual compound reactivities. The contribution of the hydrocarbon compounds to the production of photochemical ozone is related to their reaction with hydroxyl radicals and ozone in the complex photooxidation mechanism. For most hydrocarbons, the OH radical is the most important reaction pathway. While a species may have a high concentration at a given site, if it is not highly reactive with the hydroxyl radical, then it does not play as important a role as a precursor to ozone formation as a compound with a high reaction rate. To account for the reactivity of the hydrocarbon as well as its concentration, we have adopted the method used by Chamedies et al., 1992, and Lawrimore et al., 1995, by calculating the propylene-equivalent concentration:

$$\text{Propy-Equiv (j)} = \text{Conc(j)} \frac{k_{\text{OH}}(j)}{k_{\text{OH}}(\text{C}_3\text{H}_6)}$$

Propy-Equiv(j) is a measure of the concentration of species j on an OH-reactivity based scale, normalized to the reactivity of propylene. Conc(j) is the concentration of species j in ppb of carbon, $k_{\text{OH}}(j)$ is the rate constant for the reaction between species j and OH, and $k_{\text{OH}}(\text{C}_3\text{H}_6)$ is the rate constant for the reaction between OH and propylene [Chameides et al., 1992]. The propylene-equivalent concentration is literally the concentration, in ppbC, required of propylene to yield a carbon oxidation rate equal to that of the species j. For example, if a species j had a concentration of 5 ppbC and was twice as reactive as propylene, it would have a propylene-equivalent concentration of 10 ppbC. This method is useful since it accounts for the reaction rate of a species as well as its atmospheric concentration. Table 6 lists the rate constant k multiplied by 10^{12} for the gas-phase reactions of the OH radical with hydrocarbons. Units of k are in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The OH rate constants for some of the hydrocarbon compounds could not be found in the literature and were therefore omitted from the propylene-equivalent hydrocarbon sums. These compounds include 3-methyl-1-pentene, 4-methy-1-pentene, cis-3-hexene,

Table 6. Rate constants k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reactions of OH radicals with hydrocarbons at $T = 298^\circ\text{K}$ (from Atkinson, 1990, except where noted).

Compound	$10^{12} \times k$	Compound	$10^{12} \times k$
Ethene	8.52	2,4-Dimethylpentane	5.1
Acetylene	0.9	1,1,1-Trichloroethane [†]	0.0119
Ethane	0.268	Benzene	1.23
Propene	26.3	Cyclohexane	7.49
Propane	1.15	2,3-Dimethylpentane	
Isobutane*	2.5	Trichloroethylene [†]	2.36
Isobutene*	51	Methylcyclohexane	10.4
1-Butene*	31.4	2,3,4-Trimethylpentane	7
n-Butane	2.54	Toluene	5.96
Trans-2-butene	64	n-Octane	8.68
Cis-2-butene	56.4	Perchloroethylene [†]	2.16
3-methyl-1-Butene	31.8	Ethylbenzene	7.1
Isopentane*	3.1	p-Xylene	14.3
1-Pentene	31.4	m-Xylene	23.6
2-methyl-1-Butene	61	Styrene [†]	5.71
n-Pentane	3.94	o-Xylene	13.7
Isoprene	101	Isopropylbenzene	6.5
Trans-2-pentene	67	a-Pinene	53.7
Cis-2-pentene	65	n-Propylbenzene	6
2-methyl-2-Butene	68.9	1-ethyl-3-Methylbenzene [†]	22.4
3-methyl-1-Pentene		1-ethyl-4-Methylbenzene [†]	13.6
4-methyl-1-Pentene		1,3,5-Trimethylbenzene	57.5
Cyclopentane	5.16	1-ethyl-2-Methylbenzene [†]	13.2
2-Methylpentane	5.6	b-Pinene	78.9
3-Methylpentane	5.7	1,2,4-Trimethylbenzene [†]	37.23
n-Hexane	5.61	Limonene	170
Cis-3-hexene		1,3-Diethylbenzene	
Methylcyclopentane [†]	6.596	n-Butylbenzene	

* Warneck 1988

[†] Middleton and Stockwell, 1990

[‡]NIST Chemical Kinetics Database, Version 5.0 [Westley et al., 1993]

2,3-dimethylpentane, 1,3-diethylbenzene and n-butylbenzene. Because these compounds were left out, the propylene-equivalent concentrations of the sums may be somewhat underestimated, though not by much since the sum of these 6 compounds range between ~ 3 and 4.5 ppbC at the four sites during the summer and between ~ 1.5 and 2 ppbC during the winter.

Figure 7 a-b shows selected hydrocarbons in propylene-equivalent concentrations. The hydrocarbon sums were calculated by first individually calculating the propylene-equivalent concentration for each hydrocarbon, then summing them up in their appropriate categories. Figure 7a shows that, by taking reactivity into account, the summer contribution of the biogenics at Candor is at least 65% of the total sum of hydrocarbons given as propy-equivalent concentrations. The biogenics include isoprene, α -pinene, β -pinene, and limonene. The biogenic contribution was highest at the Centreville site, contributing 90% to the total sum. The biogenics at the Oak Grove and Yorkville sites represented 78% and 69% of the total, respectively. Isoprene was clearly the dominant compound during the summer, having a propylene-equivalent concentration ranging from 81.22 ppbC at the Centreville site, to 37.63 ppbC at the Yorkville site. The reaction between isoprene and the hydroxyl radical is approximately 3.84 times faster than the reaction between propylene and OH. This means that at the Centreville site, for example, a concentration of 81 ppbC of propylene would be required to yield a carbon oxidation rate equivalent to 21 ppbC of isoprene. Also from figure 7a, the propy-equivalent concentrations for the paraffins, olefins and aromatics are much lower than the biogenic compounds. For example, the propylene-equivalent alkane sums range from 2 ppbC to 5.5 ppbC among the sites. Table 7 includes the ten most abundant species in propylene-equivalent concentrations during the summer and winter seasons for each site.

In contrast to the summer propylene-equivalent concentrations, the total propylene-equivalent nonmethane hydrocarbon sum was four to seven times lower for the winter season, ranging from 15 to 21 ppbC, as shown in figure 7b. Despite virtually negligible isoprene emissions during the winter season, the biogenics still dominate in the winter due to the emissions of terpenes throughout the year. When taking reactivity into account, limonene was the dominant terpene compound at all sites, ranging from ~3 to ~ 4

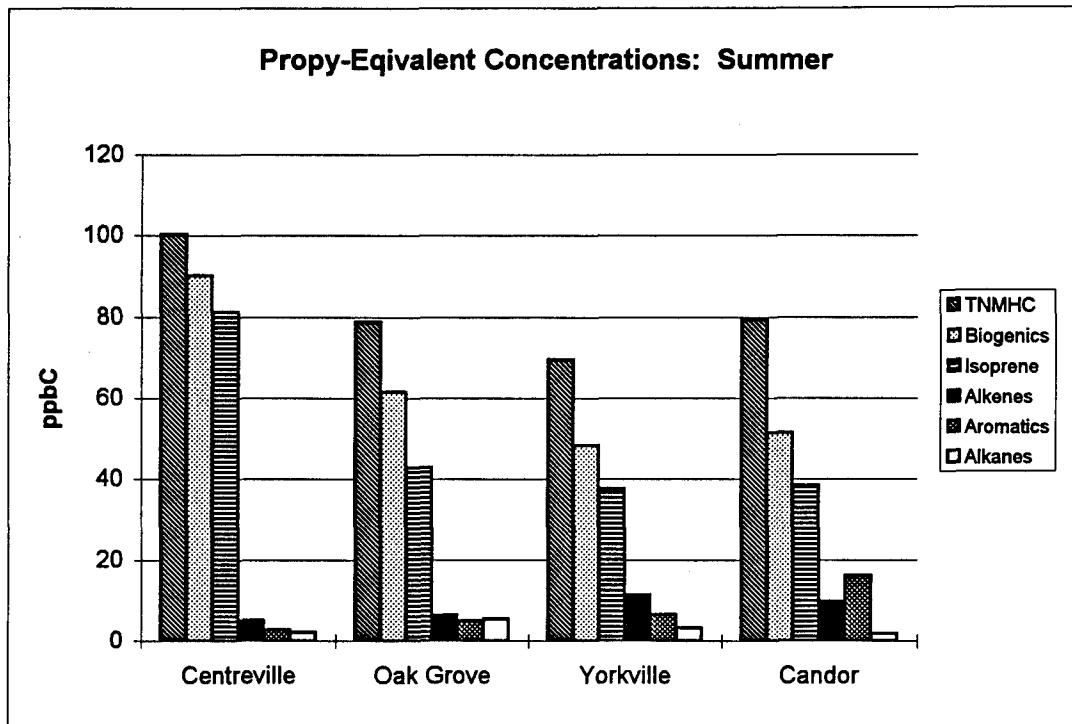


Figure 7a. Hydrocarbon sums calculated in propylene-equivalent concentrations for the summer season. Biogenics include isoprene, α -pinene, β -pinene, and limonene.

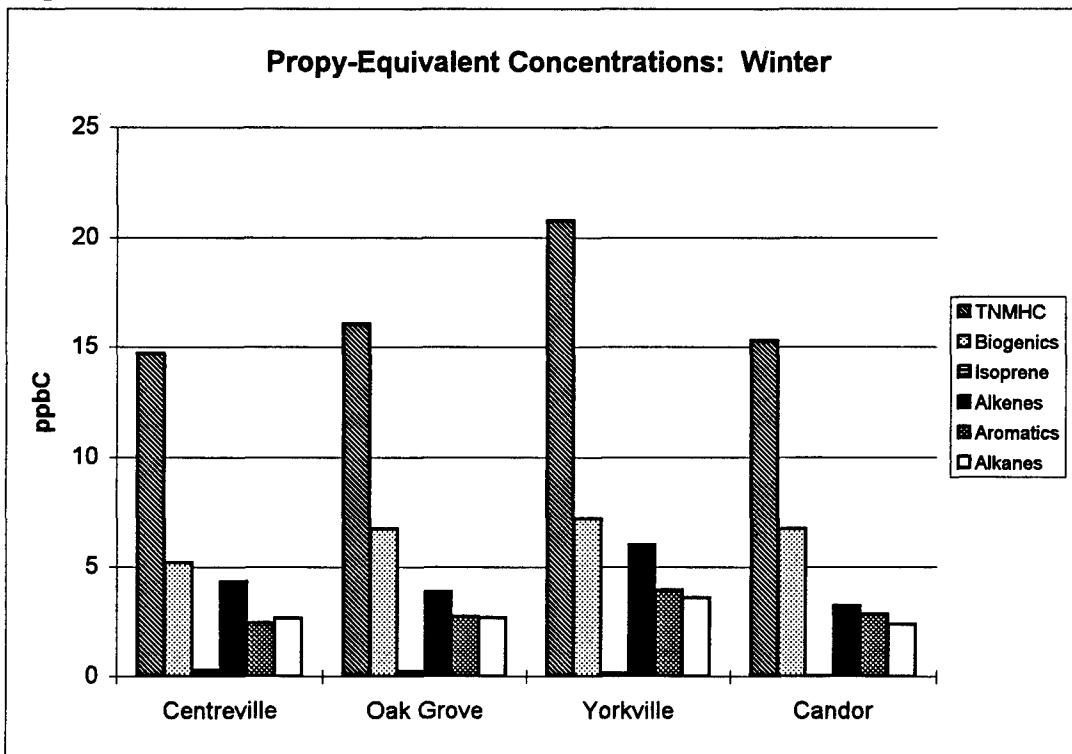


Figure 7b. Hydrocarbon sums calculated in propylene-equivalent concentrations for the winter season.

Table 7. Ten dominant hydrocarbons calculated in propylene-equivalent concentrations, listed in descending order.

Ten dominant propylene-equivalent summer concentrations									
Centreville		Oak Grove		Yorkville		Candor			
Isoprene	81.22	Isoprene	42.98	Isoprene	37.63	Isoprene	38.48		
b-Pinene	4.07	b-Pinene	9.13	b-Pinene	6.19	1,2,4-Trimethylbenzene	9.62		
a-Pinene	3.26	a-Pinene	5.53	Trans-2-pentene	3.67	a-Pinene	4.59		
iso+1butene	3.00	Limonene	4.05	Limonene	3.00	Limonene	4.48		
Limonene	1.55	iso+1butene	2.89	1-Pentene	2.28	b-Pinene	3.90		
1,2,4-Trimethylbenzene	1.04	n-Pentane	2.47	Isobutene+1-Butene	2.21	Trans-2-butene	3.48		
Propene	0.73	1,2,4-Trimethylbenzene	1.01	Propene	1.61	2-methyl-2-Butene	2.27		
2-Methylpentane	0.71	Trans-2-pentene	0.96	1,3,5-Trimethylbenzene	1.61	iso+1butene	1.81		
1-Pentene	0.43	1,3,5-Trimethylbenzene	0.94	a-Pinene	1.44	Propene	1.75		
1,3,5-Trimethylbenzene	0.41	Toluene	0.82	1,2,4-Trimethylbenzene	1.08	1,3,5-Trimethylbenzene	1.23		

Ten dominant propylene-equivalent winter concentrations									
Centreville		Oak Grove		Yorkville		Candor			
Limonene	2.80	Limonene	3.43	Limonene	4.34	Limonene	3.20		
iso+1butene	2.12	b-Pinene	2.02	iso+1butene	2.34	b-Pinene	2.05		
b-Pinene	1.39	iso+1butene	1.88	b-Pinene	1.78	a-Pinene	1.44		
Propene	0.78	a-Pinene	1.02	Propene	1.09	iso+1butene	0.87		
a-Pinene	0.73	1,2,4-Trimethylbenzene	0.77	Ethene	0.92	Propene	0.78		
Ethene	0.64	Propene	0.56	a-Pinene	0.92	1,2,4-Trimethylbenzene	0.75		
1-Pentene	0.58	m+p xyle	0.55	1,2,4-Trimethylbenzene	0.77	Ethene	0.74		
1,2,4-Trimethylbenzene	0.51	n-Butane	0.53	m+p xyle	0.69	n-Butane	0.48		
n-Butane	0.48	Ethene	0.51	Toluene	0.68	m+p xyle	0.43		
Toluene	0.42	1-Pentene	0.49	n-Butane	0.67	Toluene	0.41		

ppbC. This is in sharp contrast to the regular concentrations, in which the alkanes dominate. While the paraffins range from 28 to 35 ppbC during the winter, their calculated propylene-equivalent concentrations are approximately 3 ppbC. It must be pointed out that the propylene-equivalent approach, or any other OH reactivity concept, prioritizes the individual compounds in terms of producing RO₂ radicals. However, the availability of NO_x is essential for the production of photochemical ozone. Also, the ozone present at these rural sites will compete with OH for the reaction with the olefin compounds, complicating the reaction mechanism of ozone production. Although the rate coefficients for reactions between olefins and ozone are much smaller than those between olefins and the OH radical, the reactions become competitive with OH when the concentration of ozone builds up (Warneck 1988, 189).

3.4. Relationship between Trace Gas and Meteorological Variables

Meteorology plays an important role in the Southeast's ozone problem. Stagnant high pressure systems often develop over the southeast in the summer and fall, which allows a steady buildup of ozone precursors. These stagnating high pressure systems often arise from the stalling of a continental high-pressure system over the Appalachian Mountains [SOS 1993, 12]. This is possibly influenced by the semi-permanent Bermuda High, which is normally located over the Atlantic Ocean [Aneja and Yoder 1992, 14].

The summer of 1993 was particularly conducive to ozone formation. June and July was dominated by a persistent circulation pattern which brought moisture from the Gulf region to the Midwest, resulting in excessive precipitation which caused severe flooding, while preventing the eastward progression of weather systems which would have brought rain and cooler weather to relieve the Southeast U.S. of drought conditions and record breaking high temperatures. The Southeast experienced the second warmest summer in 99 years of record keeping¹. For the week of July 18-24, above normal temperatures affected the area from the southeastern Plains to the middle and southern Atlantic Coast, with temperatures averaging 3° to 8° higher than normal². Abnormally hot weather continued through July 25-31³. Figures 8a-g show surface and 500 mb height contours for July 19th through the 25th. Throughout this period, an upper level high characterized by light 500 mb winds was centered over the Southeast. During the period of the ozone episode (July 20-24), a stationary blocking pattern characterized by a high amplitude ridge or an omega block was centered over the central states, then over the Mississippi valley region. An omega block is a high amplitude ridge shaped as the capital

¹ U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center. United States seasonal climate summary, summer (June-August) 1993. *Weekly Climate Bulletin*. Ed. Richard Tinker. No. 93/39. Washington DC: Govt. Printing Office, September 29, 1993.

² U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center. United States weekly climate highlights, for the week of July 18-24, 1993. *Weekly Climate Bulletin*. Ed. Richard Tinker. No. 93/30. Washington DC: Govt. Printing Office, July 28, 1993.

³ U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center. United States weekly climate highlights, for the week of July 25-31, 1993. *Weekly Climate Bulletin*. Ed. Richard Tinker. No. 93/31. Washington DC: Govt. Printing Office, August 4, 1993.

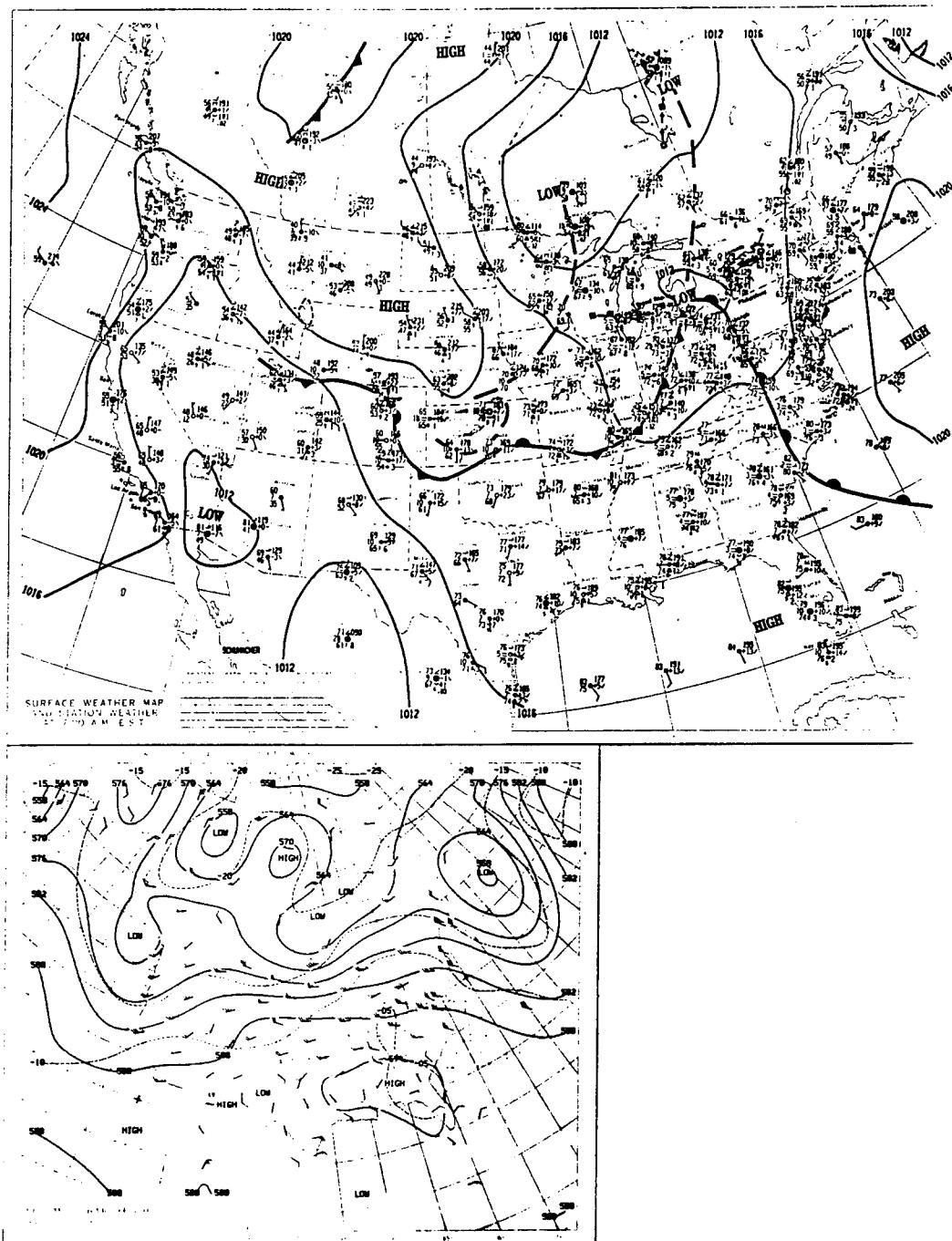
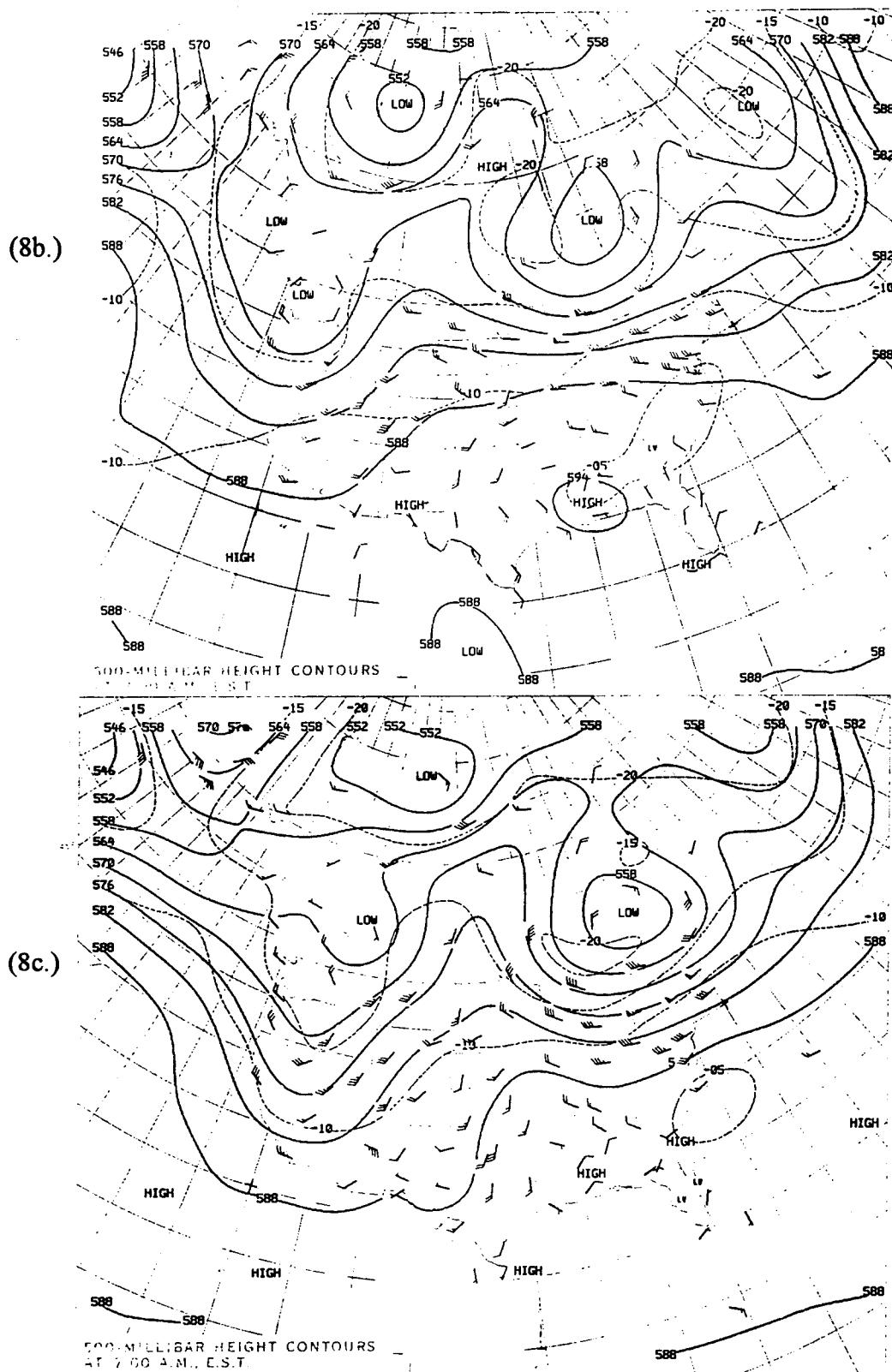
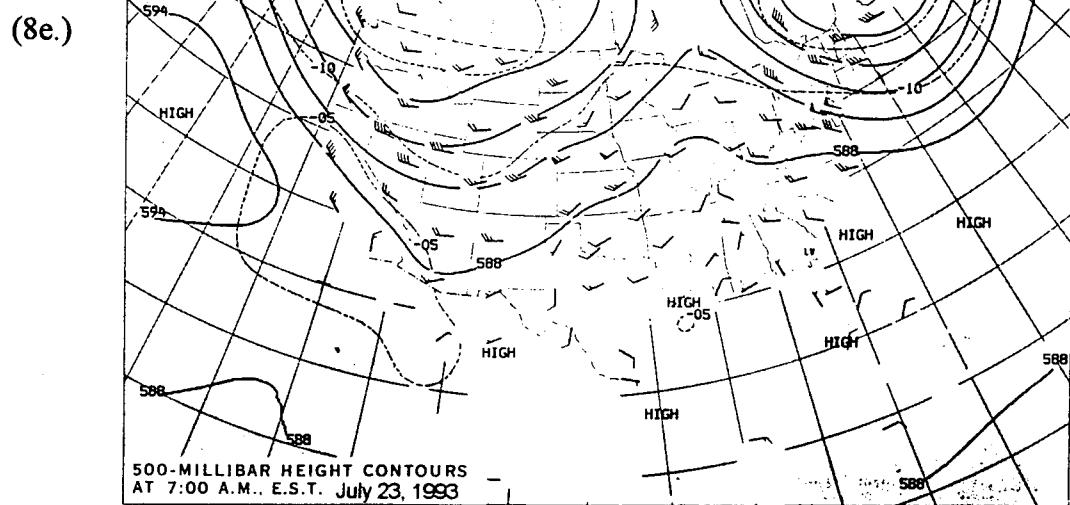
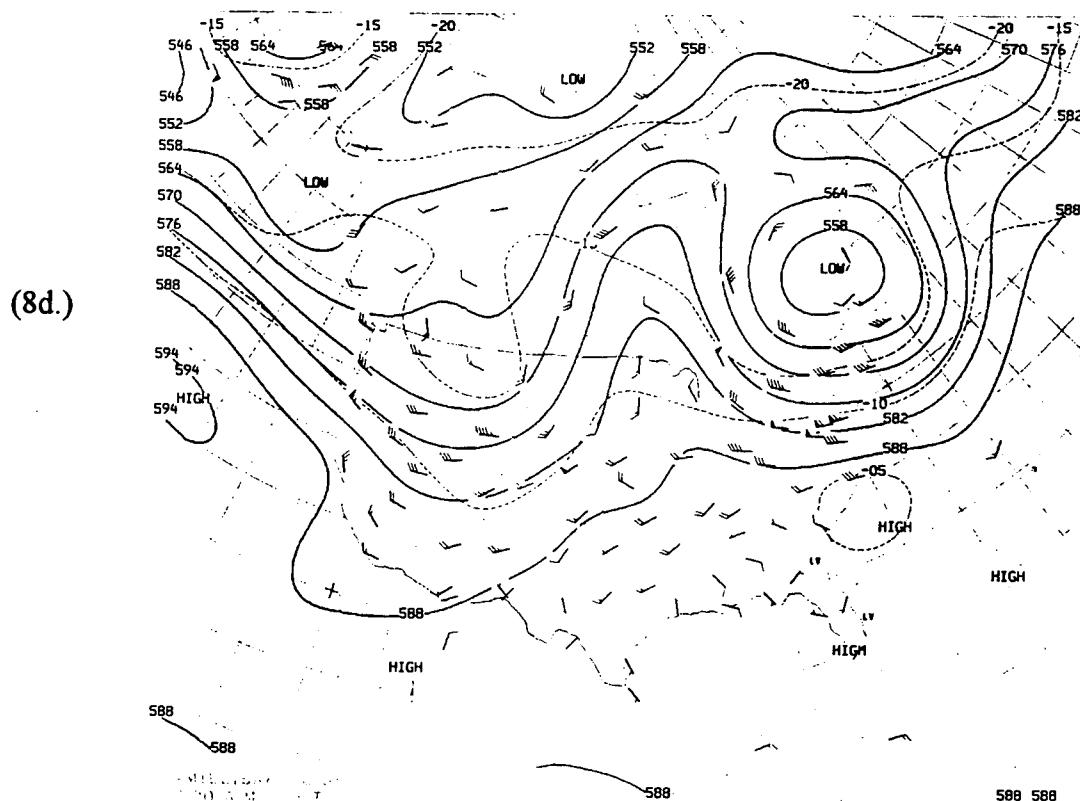


Figure 8a. Surface map and 500 mb height contours at 7am EST, Monday July 19, 1993⁴

⁴ Figures 8a-8g are taken from the National Weather Service, *Daily Weather Maps*, July 19-25, 1993.



Figures 8 b-c. 500 mb height contours at 7am EST, on (b) Tuesday July 20, 1993 (top figure) and (c) Wednesday July 21, 1993 (bottom figure).



Figures 8 d-e. 500 mb height contours at 7am EST on (d) Thursday July 22, 1993 (top figure) and (e) Friday July 23, 1993 (bottom figure).

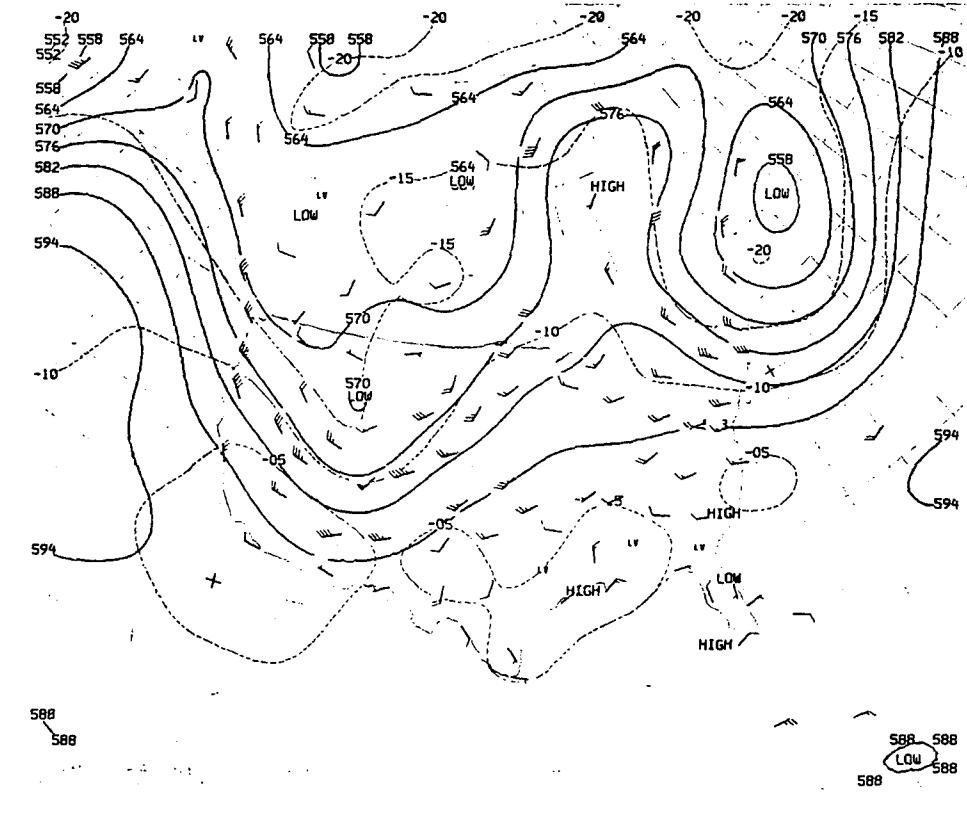


Figure 8f. 500 mb height contours at 7am EST, Saturday July 24, 1993.

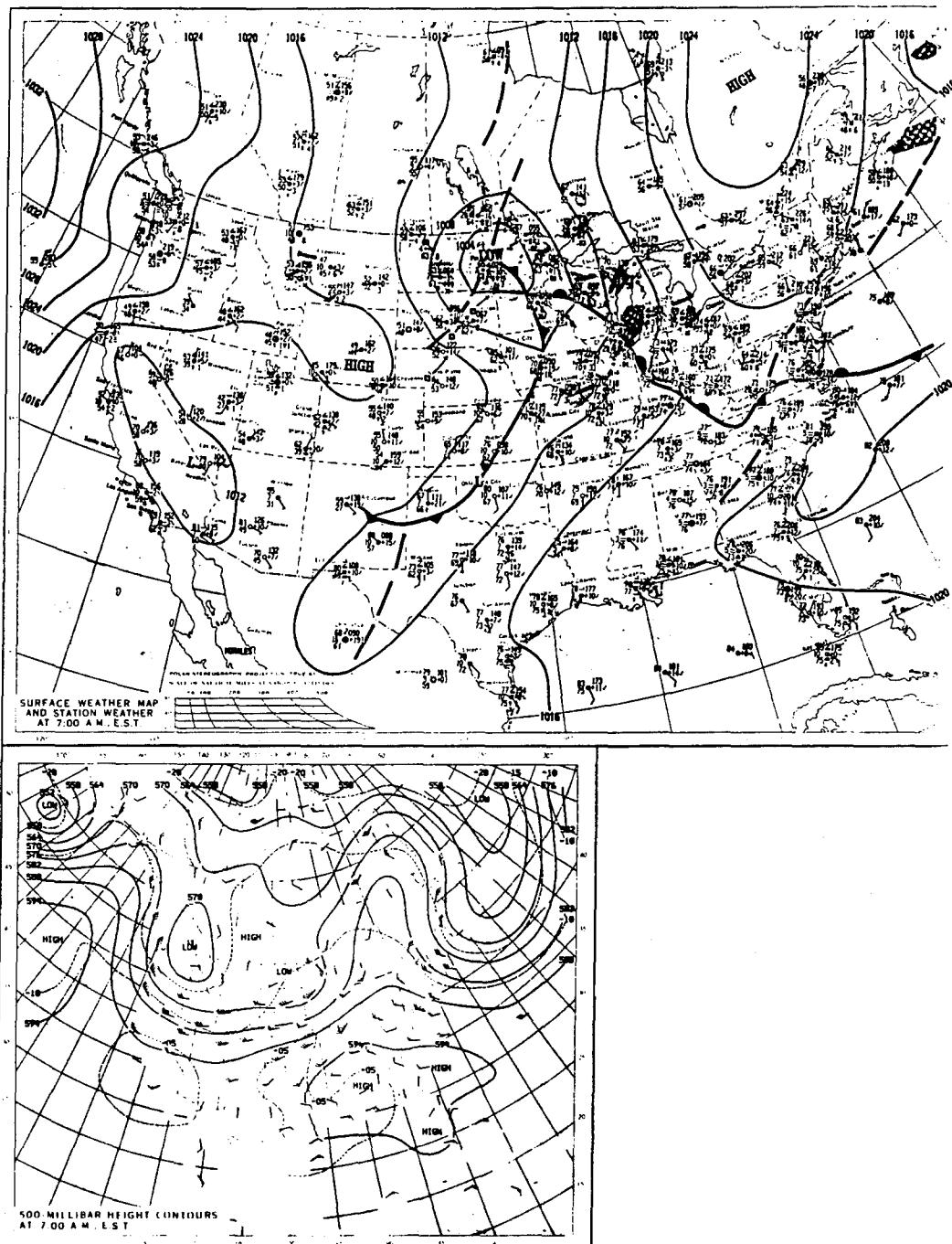


Figure 8g. Surface map and 500 mb height contours at 7am EST, Sunday July 25, 1993.

Greek letter Ω , and is sandwiched in between two lows [Bluestein 1993, 79]. In a blocking pattern, those living near upper-level cyclones tend to experience a persistent combination of precipitation and relatively cool temperatures, while those near upper-level anticyclones tend to experience drought conditions, which was the situation for this period.

Figure 9 is a plot of hourly averaged ozone during an episode which occurred from July 20th through July 25th, 1993. Ozone values for July 20th to 22nd at the Candor site are not included because of system malfunction. On July 19, a warm front passed through the southeastern Atlantic coast states. The 7 am EST surface map shows the warm front situated across Virginia, North and South Carolina. Ozone was low at all of the sites on this day (Figure 9). Yorkville received 3.8 cm of precipitation the previous evening on the 18th, and 4 cm the next morning on the 19th as a result of the frontal passage. Candor received precipitation later in the day from 10 am to 4 pm. Oak Grove also received precipitation late in the afternoon, from 4 to 5 pm. Centreville did not receive any rain during the episode. By comparing the diurnal profiles of Centreville and Yorkville, it appears that ozone at Centreville preceded that of Yorkville by approximately a day, its maximum increasing a day earlier and declining two days sooner than Yorkville. On the 20th, the high pressure center over the southeastern states, influenced by the omega block over northern Canada and upper level ridge over the mid-west, is the only distinct weather feature which would explain the increase in ozone concentrations at the Centreville and Yorkville sites. On the 21st, the omega block had moved from northern Canada down towards the central plains of the U.S., while the high pressure and high temperatures continued. Daily maximum ozone exceeded 100 at both Centreville (109 ppb) and Yorkville (108 ppb) while increasing to 54 ppb at Oak Grove. On the 22nd, the omega block became quite distinctive, having moved towards the east and centering over the Mississippi Valley. High pressure continued over the southeast with light 500 mb winds and high temperatures. Daily maximum ozone exceeded 100 ppb at both Centreville and Yorkville for a second day, reaching 104.5 ppb at Centreville and peaking at 115 ppb at Yorkville. Ozone reached 65 ppb at Oak Grove. On the 23rd and 24th, the upper level omega blocking pattern remained centered over the Mississippi Valley region. High

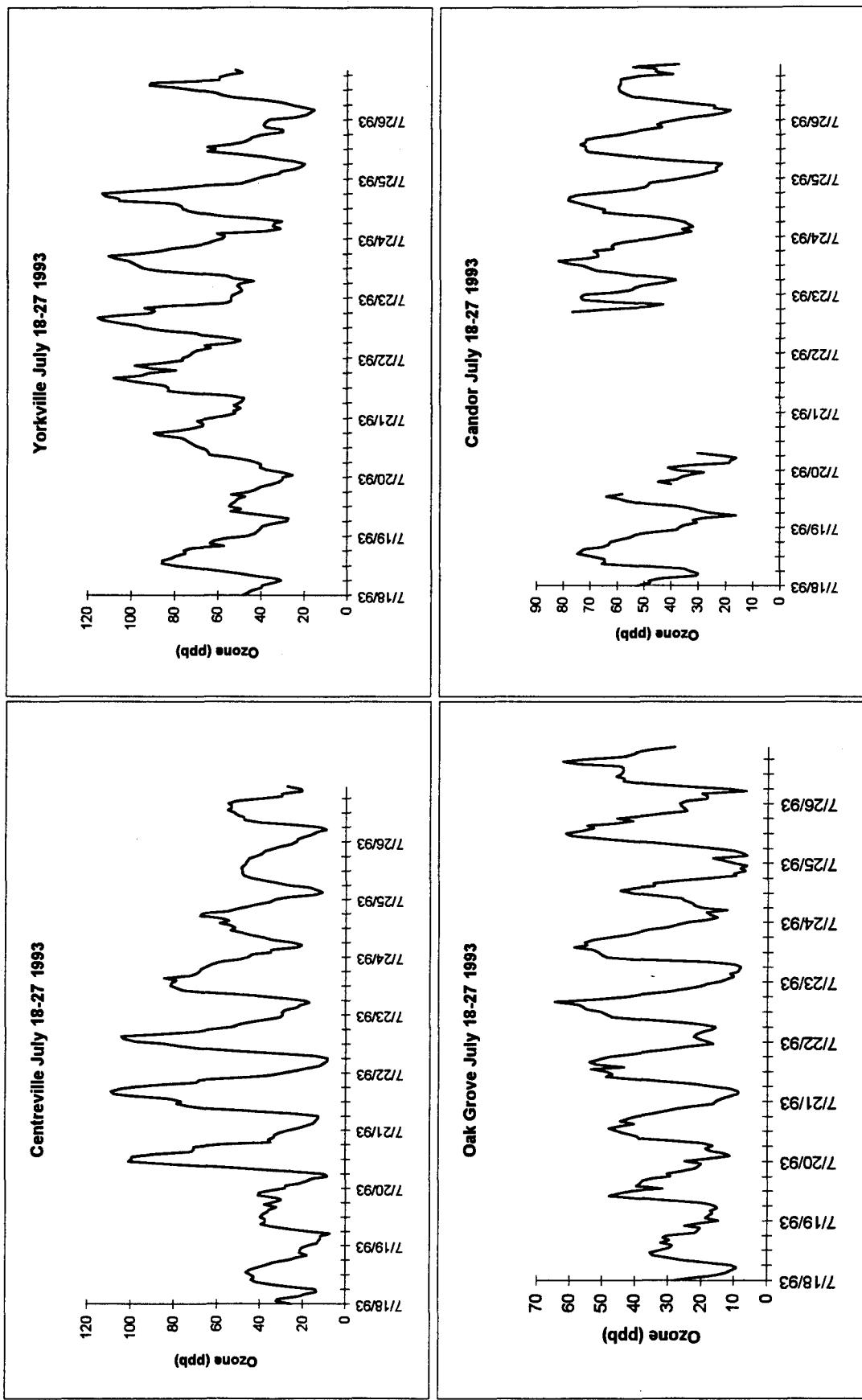


Figure 9. Diurnal profiles of ozone during an episode which occurred July 20-25 1993.

pressure and high temperatures continued in the Southeast. Daily maximum ozone on the 23rd decreased to 84.5 ppb at Centreville and to 58.75 at Oak Grove, while peaking at 110.5 ppb at Yorkville. Ozone decreased at Centreville and Oak Grove on July 24 while remaining high at Yorkville (113 ppb maximum). On July 25, a trough line shown on the NWS surface analysis shows it passing through the southeastern Atlantic coast states. Daily maximum ozone reached only 65 ppb at Yorkville, which can be explained by precipitation which occurred throughout the afternoon and evening on the previous day (July 24) and again through the afternoon and evening on the 25th. Ozone remained low at Centreville (49 ppb).

Figure 10 shows the trace gases (O_3 , CO, SO_2 , NO_y) measured at the sites during the hydrocarbon sampling period (every 6 days, 1200 to 1300). The only trace gas measured at Candor was ozone. From figure 10 we see that the Yorkville site has the highest summer average of ozone of all the sites (93 ± 22 ppb). It also has the highest CO, SO_2 , NO, and NO_y among the three sites for which measurements were taken. This indicates that Yorkville, while perhaps located in a rural site, is subject to the influence of anthropogenic emissions. Yorkville is located approximately 45 miles (72 km) west of Atlanta, Georgia, and pollutant transport is most likely the reason for these high values. The average ozone for Centreville and Oak Grove during the summer remained essentially the same as during the spring and autumn.

Table 8 shows the mean and standard deviation of the meteorological and trace gas data for the period from June 1 to August 31, 1993, using data averaged from 10 am to 4 pm for each day, using approximately 92 observations. As can be seen from Table 8, ozone was the highest at the Yorkville and Candor sites. Relative humidity, CO, SO_2 , NO, and NO_y were also highest at Yorkville. A t-test was performed for these parameters between Yorkville and Centreville, and Yorkville and Oak Grove. The t-test showed that daily average ozone at Yorkville was significantly higher than at Centreville or Oak Grove at the 1% level ($p = 0.0001$). SO_2 , NO, and CO also showed up as significantly higher at the Yorkville site ($p=0.0001$). The difference in NO_y between Yorkville and Oak Grove was significant at the 1% level, and significant at the 5% level between Yorkville and Centreville. The higher concentrations of these compounds shows that Yorkville, despite

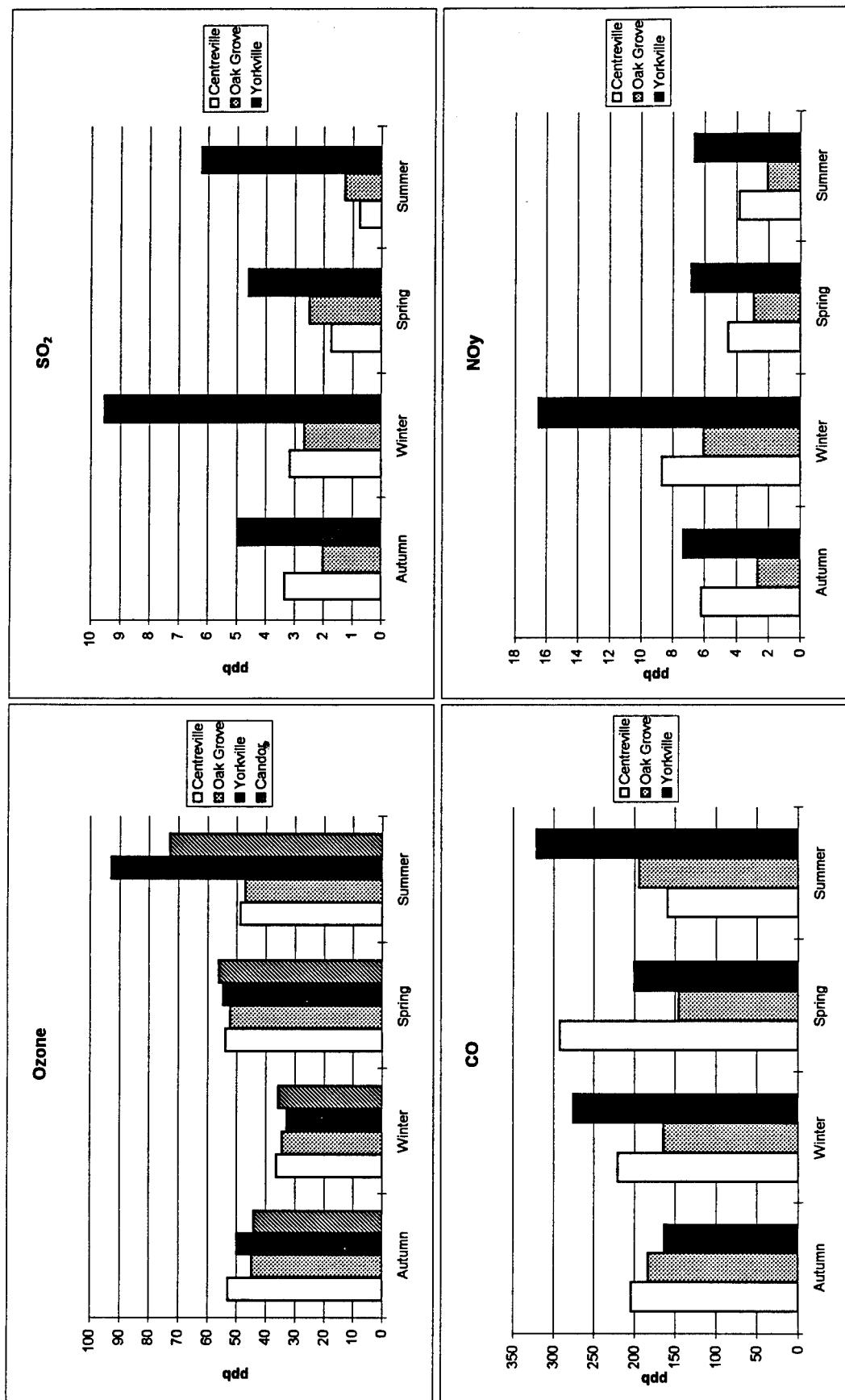


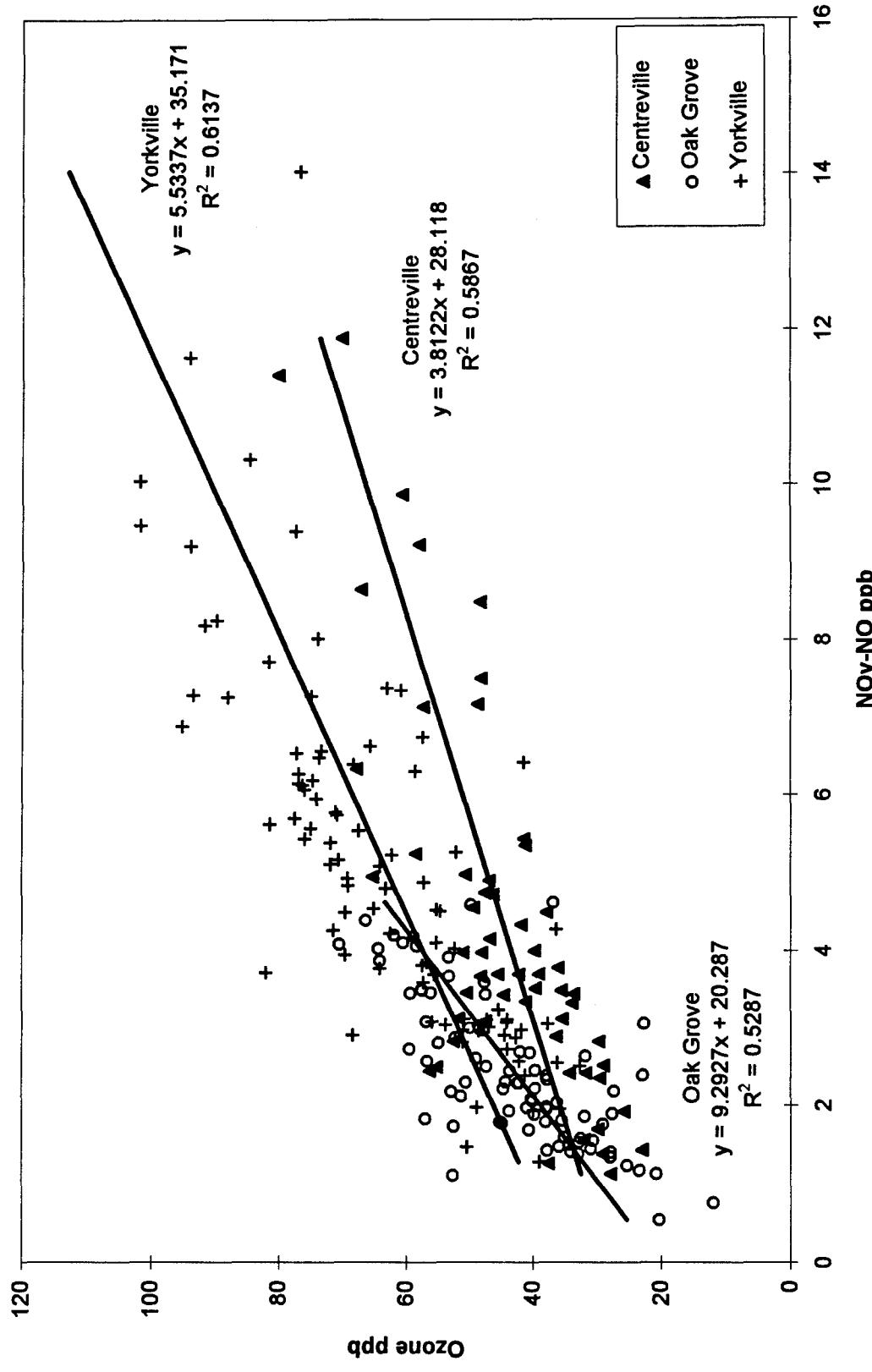
Figure 10. Seasonal averages of trace gases measured during the hydrocarbon sampling period. Ozone represents the seasonal average of daily maximum ozone.

Table 8. Descriptive statistics of meteorological and trace gas data for all four sites. The data used represents daily averages from 1000 to 1600, for the period June 1 through August 31, 1993 (n = 92). The daily max O₃ represents the maximum ozone concentration occurring between 1000 and 1600 each day.

Summer 1993	Centreville		Oak Grove		Yorkville		Candor	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
Temp (°C)	30.58	2.51	29.72	2.38	28.01	2.62	29.30	5.62
Relative Humidity	62.55	11.93	64.30	11.98	67.51	11.68	44.59	10.31
pBARO (mmHg)	746.14	2.43	754.65	1.46	728.95	1.74		
Solar Rad (w/m ²)	585.96	176.45	577.07	197.43	599.36	262.13	592.12	256.55
daily avg O ₃ (ppb)	47.57	14.66	43.63	11.92	63.47	16.58	65.00	11.54
daily max O ₃ (ppb)	56.19	17.88	51.22	13.54	76.13	22.67		
CO (ppb)	164.70	45.84	184.31	50.24	297.68	58.25		
SO ₂ (ppb)	2.11	2.58	1.95	1.84	5.39	5.94		
NO (ppb)	0.13	0.13	0.13	0.21	0.30	0.25		
NO _y (ppb)	4.47	2.48	2.58	0.98	5.42	2.41		

Table 9. Correlations between meteorological variables and trace gases. The data used are daily averages for the period June 1 through August 31, 1993. Avg O₃ is the ozone concentration averaged from 1000 to 1600 each day, and max O₃ is the daily maximum ozone concentration occurring between 1000 and 1600.

York 93	Temp	RH	pBaro	Solar	avg O ₃	max O ₃	CO	SO ₂	NO	NO _y
TEMP	1.00									
RELHUM	-0.75	1.00								
pBARO	-0.19	0.05	1.00							
SOLRAD	0.31	-0.51	-0.09	1.00						
avg O ₃	0.51	-0.44	0.03	0.00	1.00					
max O ₃	0.48	-0.41	0.07	-0.07	0.95	1.00				
CO	-0.04	0.18	-0.03	0.21	0.38	0.35	1.00			
SO ₂	0.17	-0.20	0.12	0.02	0.36	0.40	0.07	1.00		
NO	-0.14	0.05	0.23	-0.01	-0.10	-0.02	0.13	0.36	1.00	
NO _y	0.26	-0.22	0.16	-0.14	0.75	0.78	0.47	0.53	0.31	1.00



50 Figure 11. Ozone versus NO_y-NO. Data used were daily averages from 1000 to 1600, June 1 through August 31 1993 (92 observations).

its rural location, is heavily impacted by anthropogenic pollutant sources, probably as a result of its relative proximity to Atlanta, Georgia, and to the power generating station to the east. T-tests on the meteorological variables show that temperature and pressure were significantly lower at Yorkville than at the other two sites ($p=0.0001$). Solar radiation was not found to be statistically different.

Daily average ozone was plotted against the difference $\text{NO}_y\text{-NO}$ in Figure 11. Ideally, one would plot the difference $\text{NO}_y\text{-NO}_x$, where $\text{NO}_x = \text{NO} + \text{NO}_2$, because this is a direct measure of the products of the NO_x oxidation and minimizes the variability due to differences in photochemical aging of the sampled air mass [Trainer et al., 1993]. Unfortunately, NO_2 was not measured and $\text{NO}_y\text{-NO}_x$ could not be plotted, and therefore the age of the air mass was not taken into account. A correlation can be seen between ozone and $\text{NO}_y\text{-NO}$ at each site. Observed ozone at Yorkville is higher than that observed at Centreville for a given $\text{NO}_y\text{-NO}$ value. This may be explained by the fact that Yorkville is 45 miles west of a large anthropogenic area source (Atlanta, Georgia), and 30 miles west of a large power generating station, and is affected by air containing relatively unaged NO_y , which, in the presence of biogenic hydrocarbons, can result in high ozone concentrations. It can also be seen that Oak Grove is a particularly clean site, with daily average ozone values not exceeding ~ 70 ppb and $\text{NO}_y\text{-NO}$ not exceeding ~ 5 ppb, so the regression line for Oak Grove is much steeper and has a lower intercept. Earlier in this work it was shown that during the summer, the Yorkville site had lower concentrations of isoprene (Figure 5a) and non-methane hydrocarbons calculated in propylene-equivalent concentrations (Figure 7a) than at Centreville or Oak Grove, yet Yorkville had the highest concentrations of ozone. Ozone production in rural areas is typically limited by the availability of NO_x rather than hydrocarbons, since isoprene and other biogenic VOCs provide a ubiquitous source of hydrocarbon precursors for ozone production. The high ozone concentrations at Yorkville highlights this NO_x limited characteristic, showing that greater concentrations of reactive nitrogen (NO_y) at Yorkville play a more significant role in ozone formation than greater concentrations of highly reactive biogenic hydrocarbons (Centreville). Correlations between meteorological variables and trace gases at Yorkville

(Table 9) show that there is a strong correlation between NO_y and daily averaged ozone (0.75), and daily maximum ozone (0.78).

A multiple linear regression analysis was performed for the summer 1993 ozone values at Yorkville. The variables which were examined for the regression analysis included hourly averaged values of temperature, relative humidity, barometric pressure, solar radiation, CO, SO₂, and NO_y. The multiple regression showed that temperature, relative humidity, and NO_y together accounted for most of the variation in daily average and daily maximum ozone at a 1% significance level. For daily average ozone, the regression equation becomes

$$\text{Ozone} = 1.698(\text{Temperature}) - 0.13(\text{Relative humidity}) + 4.55(\text{NO}_y)$$

A plot of the observed ozone values and predicted values based on the above equation is shown in Figure 12. As you can see, the estimated ozone values follow the actual values rather well, the only exception to this being the erroneously high prediction on August 11th, which is due to a daily averaged NO_y spike of 14.26 ppb. The R-squared value of this regression was reported in the output of the SAS statistical program to be 0.978, though it must be noted that this R-squared value is misleading. The intercept was removed from the equation because it was not statistically significant at the 5% level, however, the absence of the intercept term causes the total sum of squares to become extremely large (i.e.: $\text{SS}(\text{total}) = \sum(y_i - \bar{y})^2$ becomes $\text{SS}(\text{total}) = \sum(y_i)^2$) and the R-squared value approximates to 1 ($R^2 = 1 - [\text{SS}(\text{error})/\text{SS}(\text{total})]$). Therefore, for the purpose of obtaining an accurate R-squared value, the multiple regression was re-evaluated with the intercept term included in the model. This yielded an R-squared value of 0.66, though the intercept was still not statistically significant, and its inclusion in the model resulted in the relative humidity parameter being not significant at the 5% level. There was virtually no change in the predicted ozone output between the two regression equations, so $R^2 \approx 0.66$ is used here as an approximate R-squared value for the regression equation reported above.

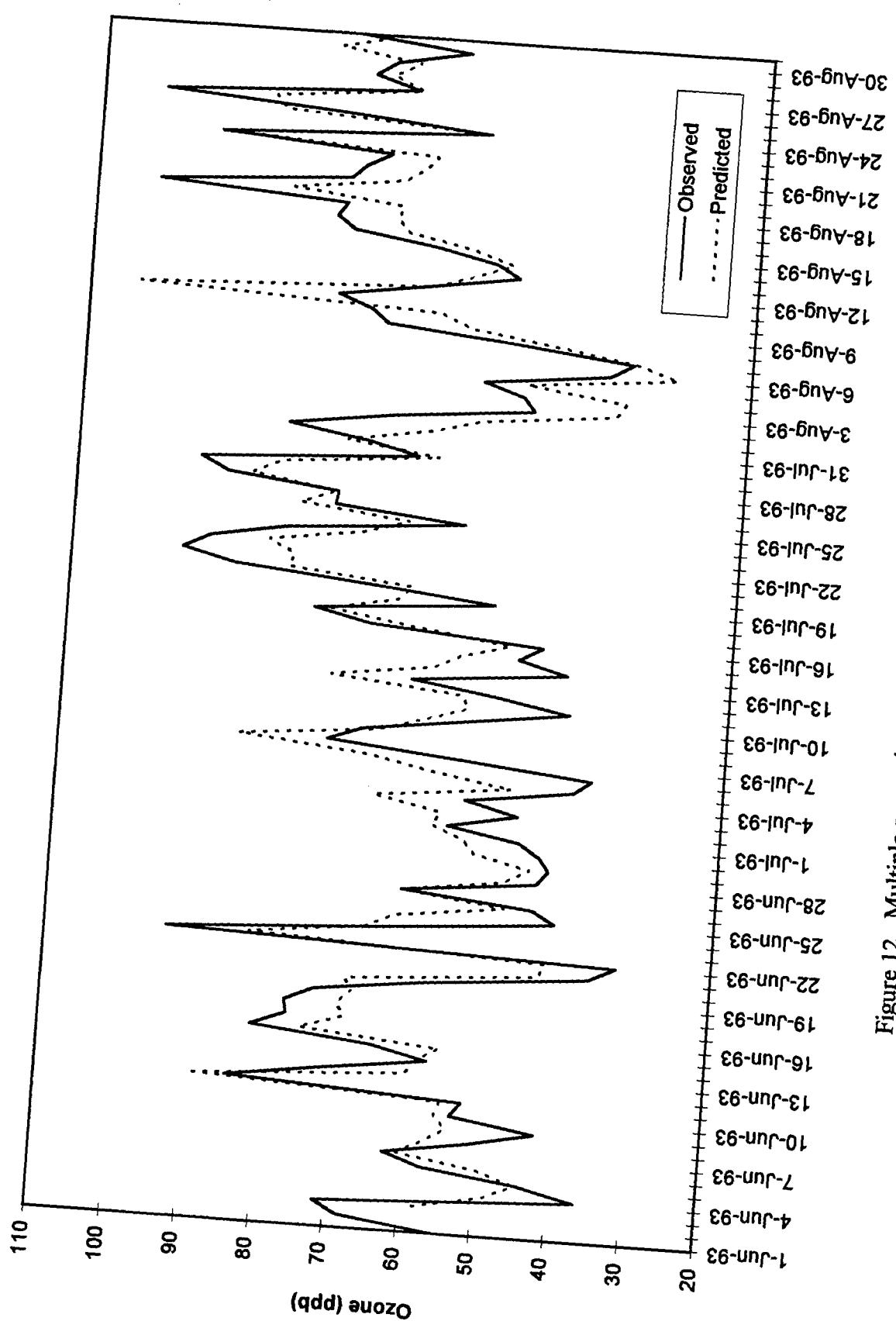


Figure 12. Multiple regression of ozone at Yorkville, summer 1993

Because Yorkville has greater concentrations of anthropogenic compounds than Oak Grove, a separate multiple linear regression was done for the Oak Grove data to compare parameter estimates. Temperature, relative humidity and NO_y were found highly significant in the linear regression of daily average ozone at Oak Grove as well. For both the Yorkville and Oak Grove regressions, temperature and NO_y were highly significant ($p = 0.0001$) while relative humidity was significant at the 5% level ($p = 0.033$ for Oak Grove and 0.037 for Yorkville). The regression equation for daily average ozone at Oak Grove was

$$\text{Ozone} = 1.181(\text{Temperature}) - 0.134(\text{Relative humidity}) + 6.497(\text{NOy})$$

which is very similar to the Yorkville regression equation.

Summary

An analysis of hydrocarbons sampled from 1992 through 1993 at four rural sites in the Southeast shows a seasonal variation of light molecular weight (C_2 - C_4) alkanes, ethene and acetylene, with a maximum during the winter and minimum during the summer. The biogenic hydrocarbons (isoprene and the terpenes) also display a seasonal variation, with a summer maximum and winter minimum. Isoprene was virtually non-existent during the winter at all sites, and averaged from 9.8 ppbC (Yorkville, GA) to 21.15 ppbC (Centreville, AL) during the summer. The terpene concentration was greatest in the summer with averages ranging 3.19 ppbC (Centreville, AL) to 6.38 ppbC (Oak Grove, MS), but was also emitted during the winter months, with a range of 1.25 to 1.9 ppbC for all sites. When considering the reactivity of hydrocarbons with the OH radical, the biogenics dominate the total non-methane hydrocarbon sum, representing between 65% to 90% of TNMHCs during the summer season, while the impact of the other hydrocarbons are less important. The propy-equivalent TNMHC sums during the summer at the four sites range between 70 to 100 ppbC with isoprene being the dominant hydrocarbon; this propy-equivalent range drops during the winter season with a range of 15 to 20 ppbC, when isoprene emissions are negligible.

Seasonal averages of the trace gases show that Yorkville was the most affected by anthropogenic emissions, while Oak Grove was the cleanest of the sites. Despite the fact that Yorkville had the lowest concentration of summer propy-equivalent total NMHCs, it had the highest values of ozone, SO_2 , NO_y and CO than the other two rural sites for which measurements were taken. A plot of ozone versus NO_y -NO shows that with a given concentration of NO_y -NO, the Yorkville site had higher ozone concentrations than either the Centreville or Oak Grove sites. These observations highlight the NO_x limited characteristic of this region, namely, that because hydrocarbons are ubiquitous in this region due to natural hydrocarbon emissions, the ozone producing potential is limited to the availability of NO_x ; in this region, greater levels of NO_x play a more significant role in ozone formation than greater concentrations of reactive biogenic hydrocarbons.

A multiple regression of ozone at the Yorkville site found the input variables temperature, relative humidity and NO_y to be statistically significant in explaining the variability of ozone ($R^2 = 0.66$).

References

Aneja, V.P., Gary T. Yoder. *Characterization of Ozone Climatology in the Southeastern United States and Climate Change*. Southeast Regional Climate Center: Columbia, S.C., 1992.

Aneja and Zheng Li. Characterization of ozone at high elevation in the eastern United States: trends, seasonal variations, and exposure. *J. Geophys. Res.* 97, 9873-9888, 1992.

Andronache, C., W.L. Chameides, M.O. Rodgers and J. Martinez. Vertical distribution of isoprene in the lower boundary layer of the rural and urban southern United States. *J. Geophys. Res.* 99, 16,989-16,999, 1994.

Atkinson, Rodger. Gas-phase tropospheric chemistry of organic compounds: A review. *Atmos. Environ.* 24A, 1-41, 1990.

Bluestein, Howard B. *Synoptic-Dynamic Meteorology in Midlatitudes, Volume II: Observations and Theory of Weather Systems*. New York: Oxford University Press, 1993.

Bongsang, B., D. Martin, G. Lambert, M. Kanakidou, J.C. Le Roulley, and G. Sennequier. Vertical distribution of nonmethane hydrocarbons in the remote marine boundary layer. *J. Geophys. Res.* 96, 7313-7324, 1991.

Boudries, H., G. Toupanc and A. L. Dutot. Seasonal variation of atmospheric nonmethane hydrocarbons on the western coast of Brittany, France. *Atmospheric Environment* 28, 1095-1112, 1994.

Carey, Francis A. *Organic Chemistry*, 2nd ed. New York: McGraw-Hill, Inc., 1992.

Chameides, W.L., R.W. Lindsay, J. Richardson, and C.S. Kiang. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science* 241, 1473-1474, 1988.

Chameides, W.L., F. Fehsenfeld, M.O. Rodgers, C. Cardelino, J. Martinez, D. Parrish, W. Lonneman, D.R. Lawson, R.A. Rasumssen, P. Zimmerman, J. Greenberg, P. Middleton, and T. Wang. Ozone Precursor relationships in the ambient atmosphere. *J. Geophys. Res.* 97, 6037-6055, 1992.

Colbeck, I., and Roy M. Harrison. The concentration of specific C₂-C₆ hydrocarbons in the air of NW England. *Atmospheric Environment* 19, 1899-1904, 1985.

Das, Mita. Physico-chemical processes regulating the formation of gaseous hydrogen peroxide in the Southeastern United States. Masters Thesis. North Carolina State University, 1993.

Dimitriades, Basil. Photochemical oxidant formation: overview of current knowledge and emerging issues. *Atmospheric Ozone Research and its Policy Implications*. Ed. T. Schneider et al. Amsterdam: Elsevier Science Publishers B.V., 1989.

Farmer, Charles T., Peter J. Milne, Daniel D. Riemer, and Rod G. Zika. Continuous hourly analysis of C₂-C₁₀ non-methane hydrocarbon compounds in urban air by GC-FID. *Environmental Science and Technology* 28, 238-245, 1994.

Greenberg, J.P., and P.R. Zimmerman. Nonmethane hydrocarbons in remote tropical, continental, and marine atmospheres. *J. Geophys. Res.* 89, 4767-4778, 1984.

Hartsell, Benjamin E., Viney P. Aneja, and William A. Lonneman. Relationships between peroxyacetyl nitrate, O₃, and NO_x at the rural Southern Oxidants Study site in central Piedmont, North Carolina, site SONIA. *J. Geophys. Res.* 99, 21033-21041, 1994.

Hov, Øystein, Norbert Schmidbauer and Michael Oehme. C₂-C₅ hydrocarbons in rural south Norway. *Atmospheric Environment* 25A, 1981-1999, 1991.

Jobson, B.T., Z. Wu and H. Niki. Seasonal trends of isoprene, C₂-C₅ alkanes, and acetylene at a remote boreal site in Canada. *J. Geophys. Res.* 99, 1589-1599, January 20 1994.

Kirk, David. Environmental Science and Engineering, personal communication, March 6, 1996.

Lamb, Brian, Alex Guenther, David Gay and Hal Westberg. A national inventory of biogenic hydrocarbon emissions. *Atmospheric Environment* 21, 1695-1705, 1987.

Lawrimore, Jay H., Mita Das and Viney P. Aneja. Vertical sampling and analysis of nonmethane hydrocarbons for ozone control in urban North Carolina. *J. Geophys. Res.* 100, 22785-22793, 1995.

Lightman, P., A.S. Kallend, A.R.W. Marsh, B.M.R. Jones and S.A. Penkett. Seasonal variation of hydrocarbons in the free troposphere at mid-latitudes. *Tellus* 42B, 408-422, 1990.

Middleton, Paulette, William R. Stockwell and William P.L. Carter. Aggregation and analysis of volatile organic compound emissions for regional modeling. *Atmospheric Environment* 24A, 1107-1133, 1990.

National Research Council. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington DC: National Academy Press, 1991.

Nelson, P.F., S.M. Quigley and M.Y. Smith. Sources of atmospheric hydrocarbons in Sydney: a quantitative determination using a source reconciliation technique. *Atmospheric Environment* 17, 439-449, 1983.

Penkett, S.A., N.J. Blake, P. Lightman , A.R.W. Marsh, P. Anwyl, and G. Butcher. The seasonal variation of nonmethane hydrocarbons in the free troposphere over the North Atlantic Ocean: possible evidence for extensive reactions of hydrocarbons with the nitrate radical. *J. Geophys. Res.* 98, 2865-2885, 1993.

Rasumssen, R.A., and M.A.K. Khalil. Isoprene over the Amazon Basin. *J. Geophys. Res.* 93, 1417-1421, 1988.

Roberts, James M., Frederick C. Fehsenfeld, Shaw C. Liu, Mark J. Bollinger, Carole Hahn, Daniel L. Albritton, and Robert E. Sievers. Measurements of aromatic hydrocarbon ratios and NO_x concentrations in the rural troposphere: observations of air mass photochemical aging and NO_x removal. *Atmospheric Environment* 18, 2421-2432, 1984.

Rudolph, J., and F.J. Johnen. Measurements of light atmospheric hydrocarbons over the Atlantic in regions of low biological activity. *J. Geophys. Res.* 95, 20583-20591, 1990.

Rudolph, J, A. Khedim, and D. Wagenbach. The seasonal variation of light nonmethane hydrocarbons in the Antarctic troposphere. *J. Geophys. Res.* 94, 13039-13044, 1989.

SAS/ETS® User's Guide, Version 6, First Edition. Cary, NC: SAS Institute Inc., 1988.

Sexton, Ken, and Hal Westberg. Nonmethane hydrocarbon composition of urban and rural atmospheres. *Atmospheric Environment* 18, 1125-1132, 1984.

Singh, Hanwant B. and Louis J. Salas. Measurements of selected light hydrocarbons over the Pacific Ocean: latitudinal and seasonal variations. *Geophysical Research Letters* 9, 842-845, 1982.

Southern Oxidants Study: 1993 Data Analysis Workshop Report. Ed. Fred Fehsenfeld, James Meager, and Ellis Cowling. Raleigh NC: North Carolina State University, Southen Oxidants Study, 1994.

The State of the Southern Oxidants Study (SOS): Policy-Relevant Findings in Ozone Pollution Research 1988 - 1994. Ed. W.L. Chameides and Ellis B. Cowling. Raleigh NC: North Carolina State University, Southern Oxidants Study, 1995.

Spivakovsky, C.M., R. Yevich, J.A. Logan, S.C. Wofsy, M.B. McElroy, and M.J Prather.
Tropospheric OH in a three-dimensional chemical tracer model: an assessment
based on observations of CH_3CCl_3 . *J. Geophys. Res.* 95, 18441-18472, 1990.

Tille, K.J.W., M. Savelsberg and K. Bächmann. Airborne measurements of nonmethane
hydrocarbons over western Europe: vertical distributions, seasonal cycles of ratios
and source strengths. *Atmospheric Environment* 19, 1751-1760, 1985.

Tingey, David T. The effect of environmental factors on the emission of biogenic
hydrocarbons from live oak and slash pine. *Atmospheric Biogenic Hydrocarbons,*
Volume 1: Emissions. Ed. Joseph J. Bufalini and Robert R. Arnts. 2 vols. Ann
Arbor, Michigan: Ann Arbor Science Publishers Inc., 1981.

Trainer, M., E.J. Williams, D.D. Parrish, M.P. Buhr, E.J. Allwine, H.H. Westberg, F.C.
Fehsenfeld, and S.C. Liu. Models and observations of the impact of natural
hydrocarbons on rural ozone. *Nature* 329, 705-707, 1987.

Trainer, M., D.D. Parrish, M.P. Buhr, R.B. Norton, F.C. Fehsenfeld, K.G. Anlauf, J.W.
Bottenheim, Y.Z. Tang, H.A. Wiebe, J.M. Roberts, R.L. Tanner, L. Newman,
V.C. Bowersox, J.F. Meagher, K.J. Olszyna, M.O. Rodgers, T. Wang, H.
Berresheim, K.L. Demerjian, and U.K. Roychowdhury. Correlation of ozone with
NO_x in photochemically aged air. *J. Geophys. Res.* 98, 2971-2925, 1993.

U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center.
United States weekly climate highlights, for the week of July 18-24, 1993. *Weekly
Climate Bulletin.* Ed. Richard Tinker. No. 93/30. Washington DC: Govt.
Printing Office, July 28, 1993.

U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center.
United States weekly climate highlights, for the week of July 25-31, 1993. *Weekly
Climate Bulletin.* Ed. Richard Tinker. No. 93/31. Washington DC: Govt.
Printing Office, August 4, 1993.

U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center.
United States monthly climate summary, July 1993. *Weekly Climate Bulletin.* Ed.
Richard Tinker. No. 93/32. Washington DC: Govt. Printing Office, August 11,
1993.

U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center.
United States seasonal climate summary, summer (June-August) 1993. *Weekly
Climate Bulletin.* Ed. Richard Tinker. No. 93/39. Washington DC: Govt.
Printing Office, September 29, 1993.

U.S. Dept. of Commerce. NOAA. National Weather Service-National Meteorological Center. Climate Analysis Center. *Daily Weather Maps*. Washington DC: Govt. Printing Office, July 19-25, 1993.

U.S. Dept. of Commerce. NOAA. National Weather Service-National Meteorological Center. Climate Analysis Center. *Daily Weather Maps*. Washington DC: Govt. Printing Office, July 26-August 1, 1993.

Vaghjiani, G.L., and A.R. Ravishankara. New measurement of the rate coefficient for the reaction of OH with methane. *Nature* 350, 406-409, 1991.

Warneck, Peter. *Chemistry of the Natural Atmosphere*. San Diego: Academic Press, Inc., 1988.

Westly, F., D.H. Frizzell, J.T. Herron, R.F. Hampton, and W.G. Mallard. *National Institute of Standards and Technology Chemical Kinetics Data Base, Version 5.0*, 1993.

SECTION II

MULTIPLE REGRESSION OF OZONE USING TRACE GAS AND METEOROLOGICAL VARIABLES WITH AUTOREGRESSIVE MOVING AVERAGE (ARMA) TIME SERIES ERRORS

1. Introduction

Ozone (O_3) is an oxidant gas produced naturally in the atmosphere. In the troposphere, it is produced when nitrogen dioxide (NO_2) is photodisassociated and combines with molecular oxygen (O_2) to produce ozone. Since the passage of the 1970 Clean Air Act amendments, regulatory efforts to comply with the National Ambient Air Quality standard for ozone have been inadequate [NRC 1991,4]. Ozone exceedences continue to be a major problem, especially in the southeast region of the United States which is characterized by high frequency of stagnating high pressure systems and significant emissions of naturally produced hydrocarbons (SOS 1995, 12).

Many studies have attempted to model the formation of ozone using highly complex computer simulations of chemical reactions of ozone precursors [Chameides et al., 1988; Trainer et al., 1987]. Highly involved models incorporating atmospheric chemistry as well as meteorological variables are necessary for accuracy. However, it is interesting to determine if a statistical model using observed ozone concentrations and meteorological input parameters at a given site can simulate ozone concentrations for another year with moderate accuracy.

In this work, a multiple regression using meteorological and trace gas data as input parameters and ARMA (autoregressive moving average) time series errors was applied to model daily average ozone. The data used was collected from June 1 through August 31

1992 at Yorkville, a rural site located in Paulding County, Georgia ($33^{\circ}55'41''$ N, $85^{\circ}02'46''$ W). This statistical model was then applied to the same site for the 1993 summer, and the predicted and observed ozone values were compared using statistical tests.

2. Time Series Review: Autoregressive moving average (ARMA) processes

Autocorrelation is the correlation of a variable with itself between the variable sampled at time t and later at time $t + \text{lag}$ (the correlation between Y_t and Y_{t+k}). When autocorrelation is zero, Y_t is a random process, while perfect correlation is denoted by a +1 or -1. The correlation between Y_t and Y_{t+k} is calculated by the autocorrelation function:

$$\rho_k = \frac{\text{Cov}(Y_t, Y_{t+k})}{\sqrt{\text{Var}(Y_t)} \sqrt{\text{Var}(Y_{t+k})}} = \frac{\gamma_k}{\gamma_0} \quad (1)$$

where $\gamma_0 = \text{Var}(Y_t) = \text{Var}(Y_{t+k})$

γ_k is called the autocovariance function, and ρ_k is called the autocorrelation function (ACF). They represent the covariance and correlation between Y_t and Y_{t+k} from the same process separated only by a time lag of k .

A time series process can be expressed in two ways: as an autoregressive representation (AR), and as a moving average (MA) representation. An autoregressive (AR) process is when a series Y_t can be predicted using past values (Y_{t-1}, Y_{t-2}, \dots) plus a random shock (e_t), such as a weather forecast for tomorrow can be predicted based on its pattern today and yesterday, with a given amount of uncertainty. A first order autoregressive process includes one past value of Y_t , and the following equation is an example of an AR(1) process:

$$Y_t = \alpha_1 Y_{t-1} + e_t \quad (2)$$

where the α_1 coefficient is the weight of the past value, and e_t is the random error.

A moving average (MA) representation is when the process Y_t is represented as a linear combination of a sequence of uncorrelated random variables, taking a weighted average of the errors where past errors are less important. A first order MA process includes one lagged error term:

$$Y_t = e_t - \beta_1 e_{t-1} \quad (3)$$

The ARMA (p,q) model is a mix of the AR and MA processes together in the same equation, where p is the order of the AR process and q is the order of the MA process.

The ARMA (1,1) model is written as

$$Y_t - \alpha_1 Y_{t-1} = e_t - \beta_1 e_{t-1} \quad (4)$$

The equation for a regression with time series errors is:

$$Y_t = \omega_0 + \omega_1 X_{1t} + \omega_2 X_{2t} + \dots + \omega_k X_{kt} + Z_t \quad (5)$$

where X_{1t} , X_{2t} , etc., are input variables and ω_1 , ω_2 ... are the unknown coefficients. Z_t is an ARIMA time series. This is a typical regression model, except that it allows for autocorrelation in the error term Z . In this work, an ARMA(1,1) equation was used for the error term Z .

3. Results and Discussion

The descriptive statistics and correlation coefficients of the ozone, trace gas and meteorological data from the Yorkville site during summer 1992 are displayed in tables 1 and 2, respectively. The data was averaged from 10 a.m. to 4 p.m. local standard time for each day, except for max O_3 , which represents the daily maximum ozone concentration.

Yorkville is affected by two potential emission sources; the city of Atlanta, located approximately 45 miles southeast of the site, and a large power generating station located approximately 30 miles east of the site [Kirk 1996].

Table 1. Descriptive statistics of the Yorkville 1992 data

Yorkville 1992	Mean	Std Error	Median	StDev	Count
Temperature C°	24.80	0.36	24.86	3.41	88
Relative Humidity	74.12	1.25	73.94	12.05	93
pBARO	728.86	0.29	729.20	2.78	92
Solar Radiation (watts m ⁻²)	539.70	22.11	563.26	182.33	68
Ozone (ppb)	50.25	1.55	49.70	14.80	91
Max Ozone (ppb)	60.07	1.80	59.00	17.07	90
CO (ppb)	204.42	5.01	204.56	47.77	91
SO ₂ (ppb)	4.98	0.66	2.66	6.29	92
NO (ppb)	0.85	0.14	0.44	1.31	93
NO _y (ppb)	8.94	0.60	7.88	5.82	93

Table 2. Correlation coefficients between 1992 variables. The values in boldface indicate correlations greater than 0.50 or less than -0.60.

York 92	TEMP	RELHUM	pBARO	SOLRAD	OZONE	max O ₃	CO	SO ₂	NO	NO _y
TEMP	1.00									
RELHUM	-0.52	1.00								
pBARO	0.35	0.00	1.00							
SOLRAD	0.55	-0.88	-0.11	1.00						
OZONE	0.18	-0.67	-0.14	0.54	1.00					
max O ₃	0.15	-0.60	-0.10	0.47	0.96	1.00				
CO	-0.25	0.17	-0.16	-0.33	0.19	0.22	1.00			
SO ₂	-0.16	0.00	0.13	-0.09	0.01	0.11	-0.06	1.00		
NO	-0.25	0.05	0.12	-0.17	-0.05	0.05	0.20	0.67	1.00	
NO _y	-0.09	-0.17	0.05	-0.03	0.45	0.52	0.44	0.44	0.77	1.00

NO_y is the sum of the reactive odd nitrogen species (NO_y = NO + NO₂ + organic nitrates + inorganic nitrates). There appears to be a strong negative correlation between ozone and relative humidity (-0.67), a fair correlation between ozone and solar radiation (0.54), and with reactive nitrogen NO_y (0.45). The relationship between ozone and meteorology is consistent with the literature. For example, studies have been done to determine long term ozone trends by removing the effect of meteorology [Chock et al., 1982; Kumar and Chock 1984; Korsog and Wolff, 1991]. Ozone is produced from photochemical reactions

between volatile organic compounds and oxides of nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$), and therefore is influenced by the level of NO_x and solar radiation. The negative correlation between humidity and solar radiation is high (-0.88).

The variables which were examined for the regression include temperature, relative humidity, barometric pressure, solar radiation, carbon monoxide (CO), sulfur dioxide (SO_2), and reactive nitrogen (NO_y). Nitric oxide (NO) was not used since NO_y includes NO ($\text{NO}_y = \text{NO} + \text{NO}_2 + \text{organic nitrates} + \text{inorganic nitrates}$). A regression model with ARMA (1,1) errors was fitted to daily average ozone for the period June 1 - August 31 1992 (refer to Appendix A for SAS programming and computer output). The model is

$$Y_t = -0.758RH_t + 0.137P_t + 0.577SO_2t + 1.053NO_yt + Z_t \quad (6)$$

$$\text{where } Z_t = 0.875Z_{t-1} + e_t - 0.662e_{t-1}$$

Y_t is daily average ozone, RH is relative humidity, P is barometric pressure, SO_2 and NO_y are sulfur dioxide (SO_2), and reactive nitrogen (NO_y), respectively. Temperature, solar radiation, carbon monoxide and an intercept term was not found to be statistically significant in explaining the variation in ozone when taking into account the other variables. Figure 1 shows the observed ozone values plotted with the predicted ozone using equation 6 above. The predicted ozone values follow the actual values very well. The observed ozone concentrations was well within the predicted 95% confidence interval, and the small values of the chi-squared statistic and high probability values (>0.05) in the autocorrelation check of residuals and shows that the residuals are white noise, indicating that the regression model fits well (refer to Appendix A, section II).

Equation 6 was next applied to the 1993 Yorkville data by using Proc ARIMA to input the values given from the 1992 regression (see Section I, Appendix B for programming). The option "noest" was used to prevent SAS from estimating a new model. As can be seen from Figure 2, the actual daily average ozone was underpredicted most of the time. Figures 3a and 3b show two plots of residuals. Figure 3a is a plot of residuals with time. The residuals tended towards the positive side of the zero axis,

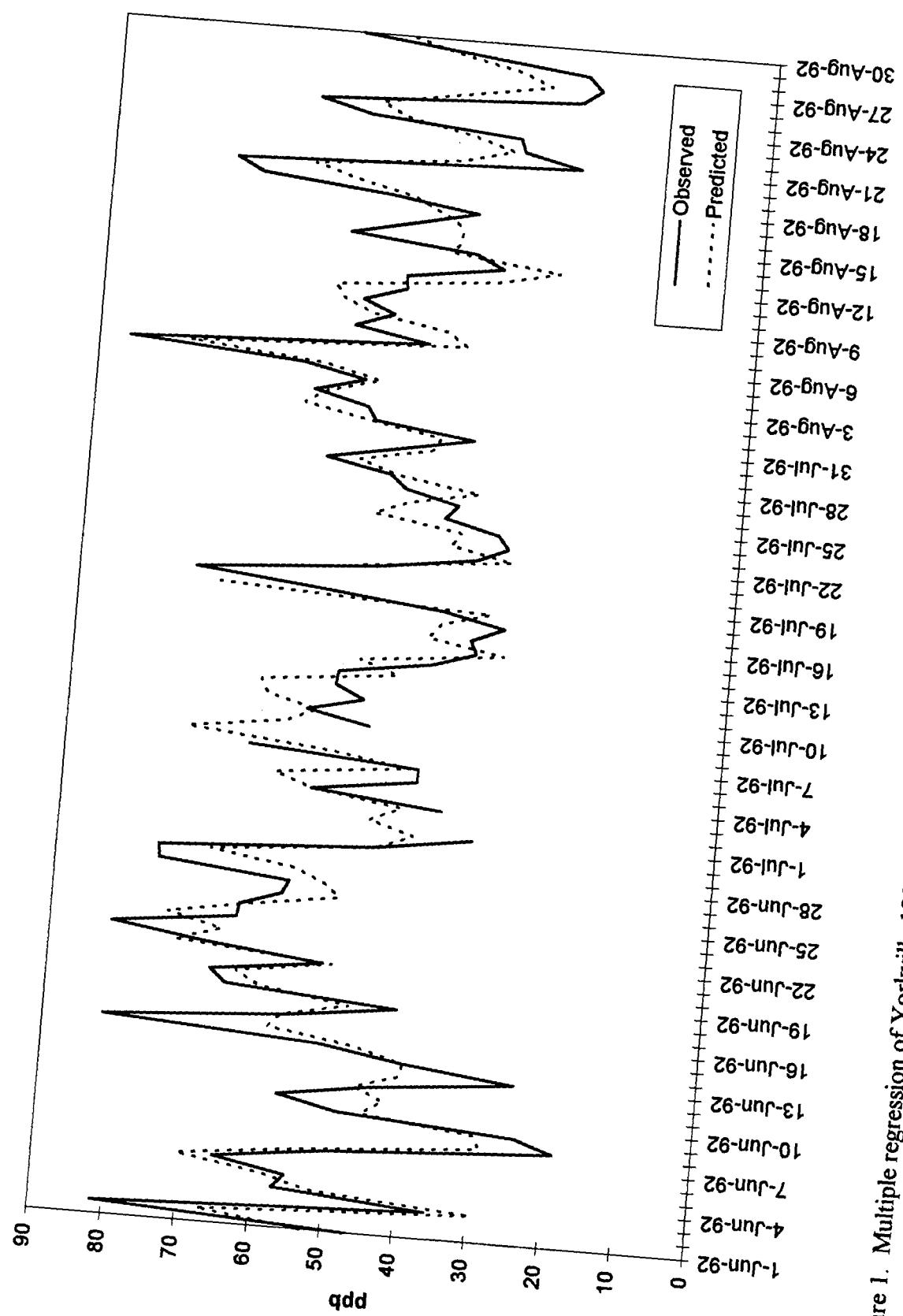


Figure 1. Multiple regression of Yorkville 1992 ozone data with ARMA errors.

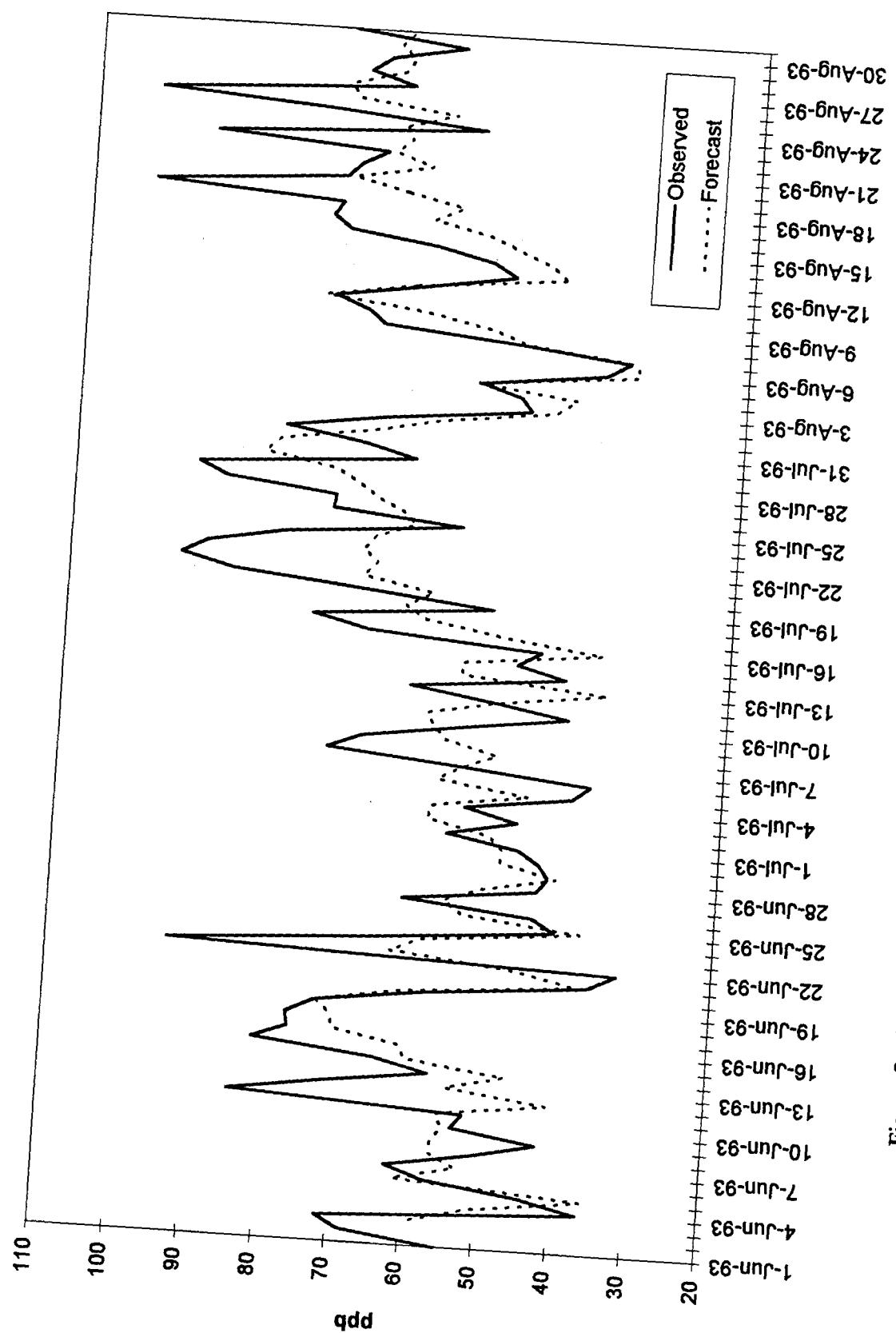


Figure 2. 1992 statistical model using 1993 data, overlayed with observed 1993 ozone

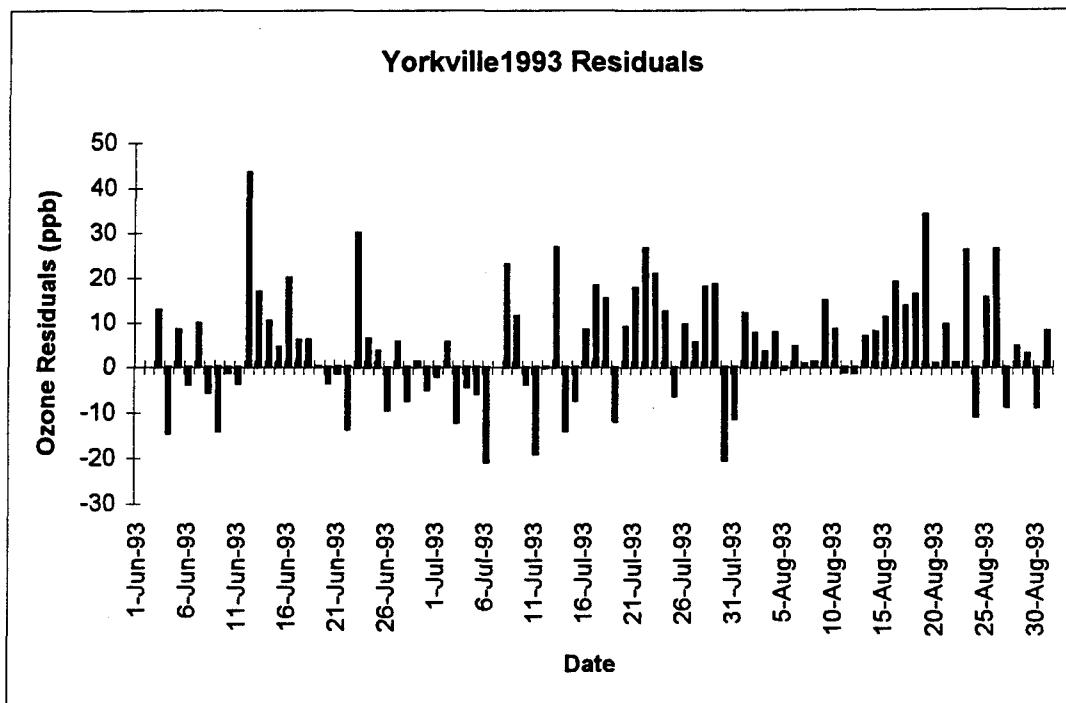


Figure 3a. Time series of ozone residuals (actual-observed)

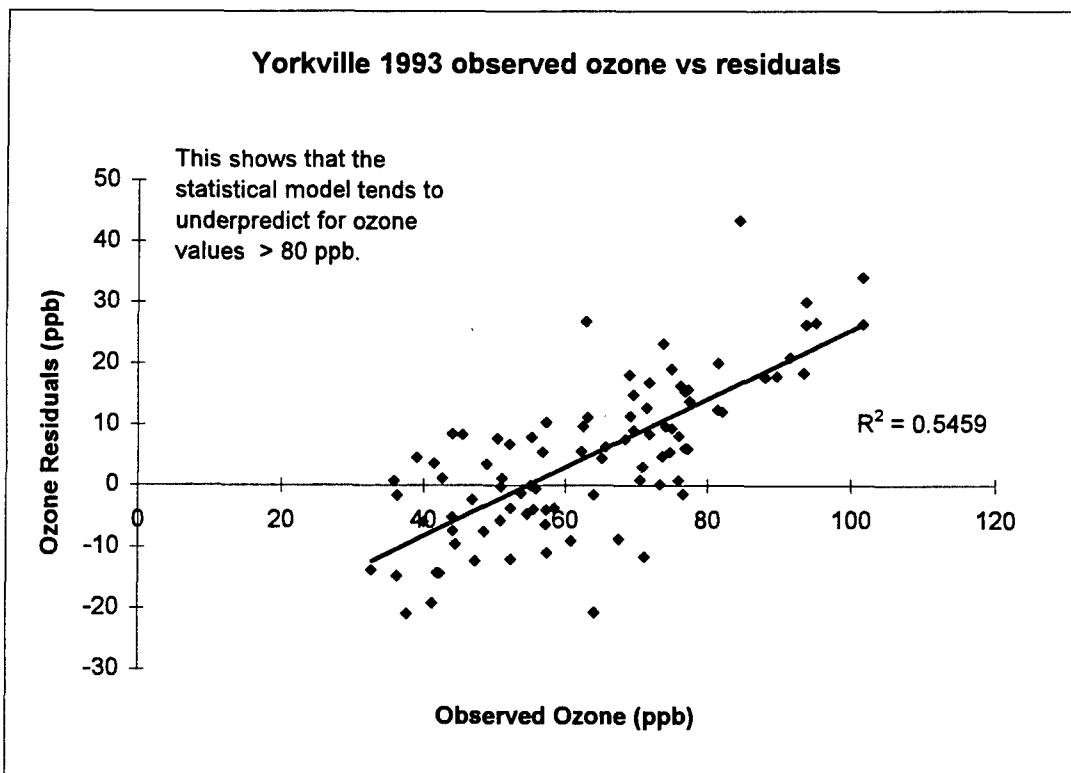


Figure 3b. Observed 1993 ozone versus residuals

having values as high as 43 ppb. A plot of residuals versus predicted ozone in figure 3b shows a linear relationship. Ozone was underpredicted for actual values greater than 80 ppb. An examination of the SAS output shows a significant chi-squared statistic and low probabilities ($p<0.05$) in the autocorrelation check of residuals, indicating that the model does not fit well and that the residuals are not white noise (Appendix B, Section II). The mean of the residuals (actual ozone - forecast ozone) is 4.91, and a t-test on the residual mean shows a significant t-statistic of 3.68 and a probability of 0.0004, indicating that the residuals are not white noise (Appendix B, Section III). The model found using the 1992 data can not be used to predict ozone using the 1993 data. A potential problem with using regression analysis is that high ozone concentrations are consistently underpredicted by the statistical model. The least-squares fitting procedure used in linear regression is designed to limit the overall mean square error, and because high ozone values (greater than 100 ppb) are extreme values and occur rarely, they might not be important in determining the regression coefficients (NRC 1991, 61). Table 3 and 4 lists the descriptive statistics and correlation coefficients, respectively, of the 1993 Yorkville data.

Table 3. Descriptive statistics of the Yorkville 1993 data

Yorkville 1993	Mean	Std Error	Median	Std Dev	Count
Temperature	28.01	0.28	28.63	2.62	90.00
Relative humidity %	67.51	1.23	65.04	11.68	90.00
Pressure	728.95	0.18	728.81	1.74	90.00
Solar Radiation	599.36	28.60	689.48	262.13	84.00
Ozone	63.47	1.73	63.62	16.58	92.00
maxo3	76.13	2.36	73.50	22.67	92.00
CO	297.68	6.07	295.40	58.25	92.00
SO2	5.39	0.62	3.51	5.94	92.00
NO	0.30	0.03	0.24	0.25	92.00
NOy	5.42	0.25	5.10	2.41	92.00

Table 4. Correlation coefficients between 1993 variables.

York 93	TEMP	RelHum	pBARO	Solar	Ozone	max O3	CO	SO2	NO	NOy
TEMP	1.00									
RELHUM	-0.75	1.00								
pBARO	-0.19	0.05	1.00							
SOLRAD	0.31	-0.51	-0.09	1.00						
OZONE	0.51	-0.44	0.03	0.00	1.00					
maxo3	0.48	-0.41	0.07	-0.07	0.95	1.00				
CO	-0.04	0.18	-0.03	0.21	0.38	0.35	1.00			
SO2	0.17	-0.20	0.12	0.02	0.36	0.40	0.07	1.00		
NO	-0.14	0.05	0.23	-0.01	-0.10	-0.02	0.13	0.36	1.00	
NOy	0.26	-0.22	0.16	-0.14	0.75	0.78	0.47	0.53	0.31	1.00

Temperature, daily average ozone, and carbon monoxide were found to be significantly higher in 1993 than in 1992 ($p=0.0001$). However, reactive nitrogen (NO_y) was found to be significantly lower in 1993 than in 1992 ($p=0.0001$) despite the higher ozone and carbon monoxide levels in 1993. Relative humidity was also found to be significantly lower in 1993 ($p=0.001$). Barometric pressure, sulfur dioxide (SO_2) and solar radiation was not found to be significantly different between the two years. By comparing 1992 correlations with 1993 correlations, we see that the correlation between ozone and the anthropogenic pollutants (CO, SO_2 , NO_y) is higher in 1993 than in 1992. The correlation between ozone and temperature was also higher in 1993 (0.51 in 1993 vs 0.18 in 1992).

Variations in ozone levels are highly influenced by synoptic meteorology [Vukovich et al., 1977; Vukovich, 1994; Niccum et al., 1995]. According to the National Weather Service *Weekly Climate Bulletin* (No. 92/37), the nation as a whole experienced its third coldest and third wettest summer in 1992 since records began in 1895. 1992 was the nation's coolest summer in 77 years, with temperatures below normal across the eastern two-thirds of the nation. The South experienced the second coolest summer on record, and the southern Plains and Southeast were inundated by moderate to heavy rains during this season.

In contrast to the cooler temperatures and above normal precipitation during 1992, June and July 1993 was dominated by a persistent circulation pattern, preventing the eastward progression of weather systems which would have brought rain and cooler weather to relieve the Southeast of drought conditions and record breaking high temperatures. The Southeast experienced the second warmest summer in 99 years of

record [NWS *Weekly Climate Bulletin* 93/39]. The difference in ozone levels between 1992 and 1993 is explained by the different weather patterns that dominated each summer. Ozone is positively correlated with high temperatures and negatively correlated with relative humidity; the lower ozone in 1992 is explained by the relatively lower temperatures and higher relative humidity, as well as the greater frequency of frontal passages, which tend to reduce the occurrence of high pressure systems that allow anthropogenic pollutants to accumulate. In a study by Vukovich et al. [1977], it was found that high ozone in the summer months is associated with high pressure systems, and that the largest concentrations of ozone were found on the back side of a moving high pressure system where air parcels had the largest residence time. A modeling study for western Australia by Hurley and Manins [1995] revealed that practically all high ozone days were associated with recirculation of ozone or its precursors.

A multiple input regression with ARMA(1,1) errors was next applied to the 1993 data to compare with the 1992 regression (Appendix C). The regression equation came out to be

$$Y_t = 1.629T - 0.539RH_t + 0.159CO + 0.29SO_2 + 1.025NO_y + Z_t \quad (7)$$

$$\text{where } Z_t = 0.949Z_{t-1} + e_t - 0.542e_{t-1}$$

Figure 4a shows the observed ozone overlaid with ozone predicted by equation 7. Figure 4b is a plot of residuals with predicted ozone, and the pattern of scatter is representative of white noise, indicating that the model is a good fit. The difference between the 1992 regression and this one is the addition of temperature and carbon monoxide, and the absence of barometric pressure in the 1993 model. This suggests a greater influence of anthropogenic emissions on ozone. The t-statistic for the parameter estimates of SO₂ and NO_y shows that they are not very significant in the model. While statistically it may make sense to remove them, NO_y is a direct precursor to photochemical ozone formation, and in an atmospheric chemistry perspective it makes more sense to leave it in the model. In a separate regression, NO_y was removed and the t-statistic of CO and SO₂ increased considerably (Appendix C, Section III).

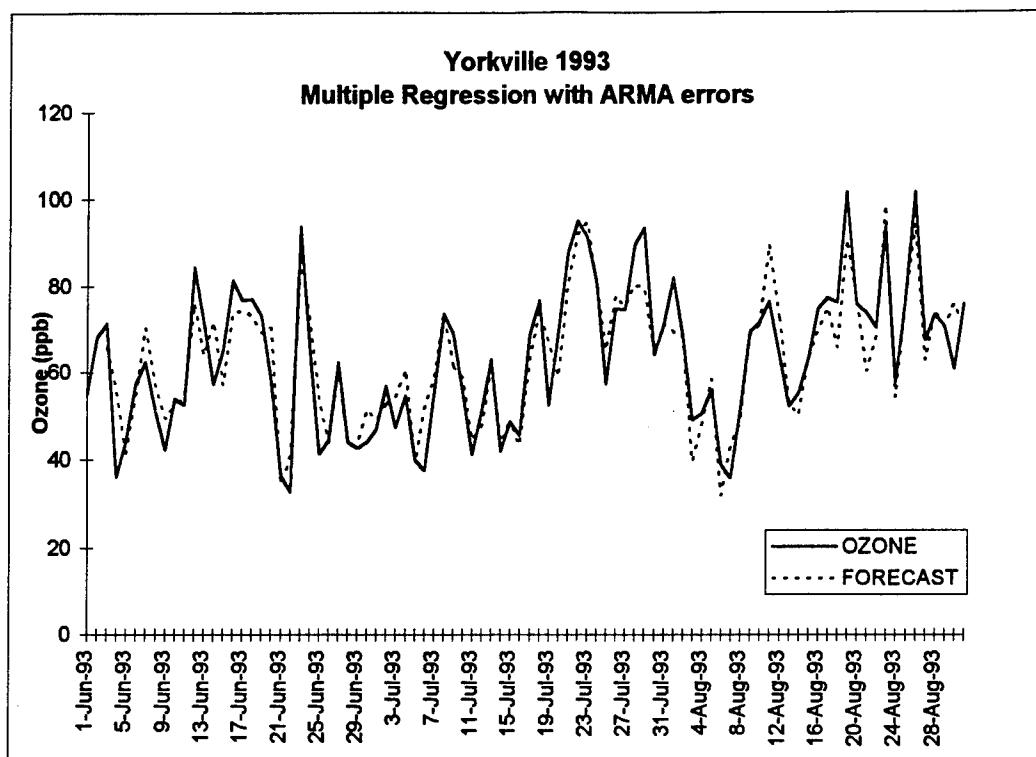


Figure 4a. Multiple regression of Yorkville 1993 ozone data with ARMA errors

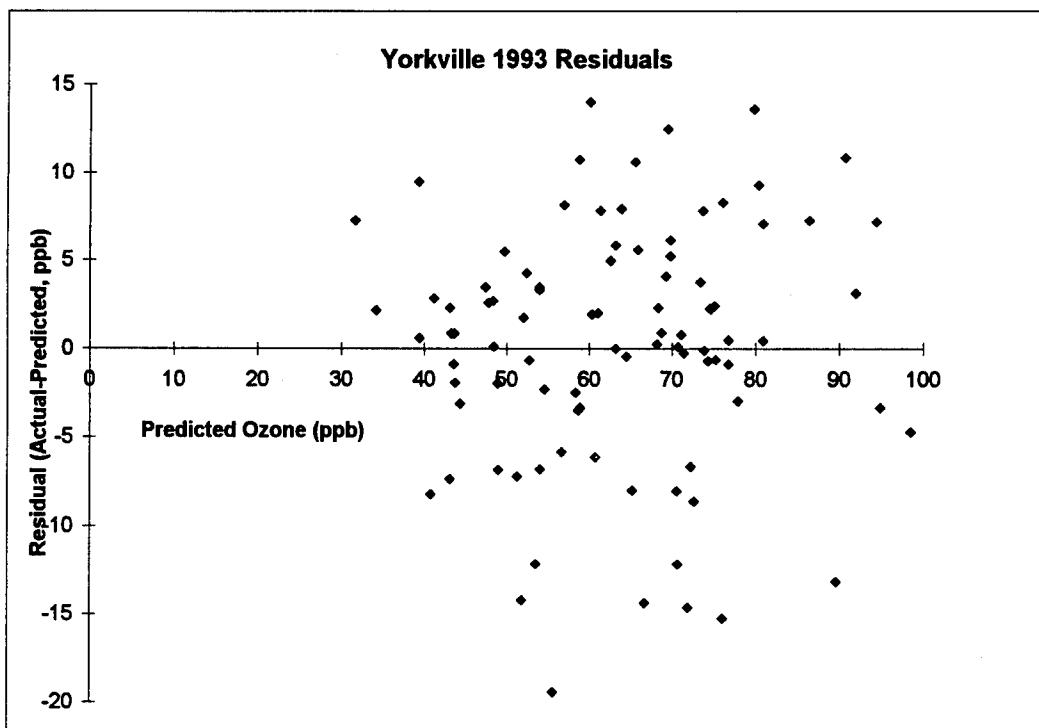


Figure 4b. Predicted ozone versus residuals for 1993 regression

Summary

A multiple regression using meteorological and trace gas data as input parameters and ARMA time series errors was applied to model daily average ozone at the rural site of Yorkville, Georgia, using data collected from June 1 through August 31 1992. This statistical model was then applied to the same site for the 1993 summer. It was found that, while a good regression model was fitted for the 1992 ozone data, the same model tended to underpredict observed ozone concentrations for the 1993 summer. Ozone was found to be statistically higher in 1993 than in 1992 (with a 1993 average of 63.5 ± 16.6 ppb and a 1992 average of 50.25 ± 14.8 ppb), and this appears to be explained by the synoptic meteorology characterizing the 1993 summer, which was conducive to high ozone formation. June and July 1993 was dominated by a persistent circulation pattern, preventing the eastward progression of weather systems which would have brought rain and cooler weather to relieve the Southeast of record breaking high temperatures and drought conditions. In contrast to the stagnant summer conditions of the 1993 summer, in 1992 the South experienced the second coolest summer on record, and the southern Plains and Southeast were inundated by moderate to heavy rains during this season. In conclusion, a multiple regression model with time series errors is not adequate to predict ozone concentrations, because other factors affecting ozone levels, such as synoptic meteorology and atmospheric chemistry, also needs to be considered.

APPENDICES

Appendix A. Multiple Regression of 1992 Ozone Data with ARMA errors

I. Program

```
goptions
  gunit=pct
  cback=white
  htitle=4
  htext=2
  ftext=swissb
  colors=(black)
  rotate=landscape;

data a;
  infile 'york92.dat';
  input Date mmddyy8. temp relhum pbaro solrad ozone maxo3 CO SO2 NO NOy;
  format Date date.;

proc arima data=a;
  identify var=ozone crosscorr=(relhum pbaro SO2 NOy) noprint;
  estimate p=1 q=1 input=(relhum pbaro SO2 NOy) noconstant plot method=ml;
  forecast lead=0 id=Date out=folder;

proc gplot data=folder;
  title 'Yorkville 1992';
  plot (forecast ozone)*Date/overlay;
  symbol1 line=2 ;
  symbol2 line=1;

proc print data=folder;
run;
```

II. Statistical Output of Yorkville 1992 Regression

ARIMA Procedure

Maximum Likelihood Estimation

Parameter	Estimate	Std Error	Approx.	T Ratio	Lag	Variable	Shift
MA1,1	0.66201	0.16512		4.01	1	OZONE	0
AR1,1	0.87511	0.10515		8.32	1	OZONE	0
NUM1	-0.75793	0.08486		-8.93	0	RELHUM	0
NUM2	0.13672	0.0097887		13.97	0	PBARO	0
NUM3	-0.57661	0.17002		-3.39	0	SO2	0
NUM4	1.05332	0.18372		5.73	0	NOY	0

Variance Estimate = 79.4084332
Std Error Estimate = 8.91114096
AIC = 641.013713
SBC = 655.877734
Number of Residuals= 88

Correlations of the Estimates

Variable	Parameter	OZONE MA1,1	OZONE AR1,1	RELHUM NUM1	PBARO NUM2	SO2 NUM3
OZONE	MA1,1	1.000	0.867	0.073	-0.109	-0.042
OZONE	AR1,1	0.867	1.000	0.021	-0.062	-0.078
RELHUM	NUM1	0.073	0.021	1.000	-0.921	0.017
PBARO	NUM2	-0.109	-0.062	-0.921	1.000	-0.022
SO2	NUM3	-0.042	-0.078	0.017	-0.022	1.000
NOY	NUM4	0.131	0.147	0.136	-0.288	-0.515

Variable	Parameter	NOY NUM4
OZONE	MA1, 1	0.131
OZONE	AR1, 1	0.147
RELHUM	NUM1	0.136
PBARO	NUM2	-0.288
SO2	NUM3	-0.515
NOY	NUM4	1.000

Autocorrelation Check of Residuals

Lag	Chi-Square	DF	Prob	Autocorrelations						
				0.054	-0.078	-0.062	-0.049	0.202	-0.017	
6	5.50	4	0.240	0.054	-0.078	-0.062	-0.049	0.202	-0.017	
12	11.92	10	0.291	0.109	-0.035	0.109	-0.073	0.004	0.175	
18	25.16	16	0.067	-0.178	0.064	-0.167	-0.072	0.185	-0.123	
24	32.81	22	0.065	-0.173	-0.143	-0.056	-0.014	-0.059	-0.082	

Autocorrelation Plot of Residuals

"." marks two standard errors

Model for variable OZONE

No mean term in this model.

Autoregressive Factors

Factor 1: 1 - 0.87511 B**(1)

Moving Average Factors

Factor 1: 1 - 0.66201 B**(1)

Input Number 1 is RELHUM.

Overall Regression Factor = -0.75793

Input Number 2 is PBARO.

Overall Regression Factor = 0.136722

Input Number 3 is SO2.

Overall Regression Factor = -0.57661

Input Number 4 is NOY.

Overall Regression Factor = 1.053324

III. Output of observed and predicted ozone, standard deviation, upper and lower 95% confidence intervals and residuals.

Yorkville 1992 Output

OBS	DATE	OZONE	FORECAST	STD	L95	U95	RESIDUAL
1	01JUN92	46.46	52.5920	9.73688	33.5080	71.6759	-6.1320
2	02JUN92	81.46	67.0483	9.22284	48.9719	85.1247	14.4117
3	03JUN92	35.76	29.3509	9.03997	11.6329	47.0689	6.4091
4	04JUN92	57.04	52.1065	8.96623	34.5330	69.6800	4.9335
5	05JUN92	55.34	58.4955	8.93503	40.9832	76.0079	-3.1555
6	06JUN92	65.40	70.3747	8.92156	52.8888	87.8607	-4.9747
7	07JUN92	49.70	53.3187	8.91570	35.8443	70.7932	-3.6187
8	08JUN92	18.81	28.9204	8.91314	11.4510	46.3898	-10.1104
9	09JUN92	24.18	29.8179	8.91202	12.3507	47.2851	-5.6379
10	10JUN92	48.88	45.5842	8.91152	28.1179	63.0505	3.2958
11	11JUN92	57.26	42.5497	8.91131	25.0839	60.0156	14.7103
12	12JUN92	44.92	46.8236	8.91121	29.3579	64.2892	-1.9036
13	13JUN92	24.78	40.6999	8.91117	23.2344	58.1655	-15.9199
14	14JUN92	40.47	40.4147	8.91117	22.9491	57.8802	0.0553
15	15JUN92	52.13	47.3188	8.91117	29.8532	64.7844	4.8112
16	16JUN92	81.83	59.2664	8.91117	41.8008	76.7320	22.5636
17	17JUN92	56.92	57.7109	8.91117	40.2454	75.1765	-0.7909
18	18JUN92	41.67	48.3452	8.91117	30.8796	65.8108	-6.6752
19	19JUN92	65.62	61.0159	8.91117	43.5503	78.4815	4.6041
20	20JUN92	67.74	64.2845	8.91117	46.8189	81.7501	3.4555
21	21JUN92	52.41	51.0400	8.91117	33.5744	68.5056	1.3700
22	22JUN92	68.88	72.9288	8.91117	55.4632	90.3944	-4.0488
23	23JUN92	81.63	66.5668	8.91117	49.1013	84.0324	15.0632
24	24JUN92	64.81	74.2631	8.91117	56.7975	91.7287	-9.4531
25	25JUN92	64.44	63.6685	8.91117	46.2029	81.1341	0.7715
26	26JUN92	58.90	50.8632	8.91117	33.3977	68.3288	8.0368
27	27JUN92	57.88	53.0958	8.91117	35.6302	70.5614	4.7842
28	28JUN92	75.90	57.2029	8.91117	39.7374	74.6685	18.6971
29	29JUN92	76.08	69.0518	8.91117	51.5862	86.5174	7.0282
30	30JUN92	46.46	46.4082	8.91117	28.9426	63.8738	0.0518
31	01JUL92	33.26	41.3676	8.91117	23.9021	58.8332	-8.1076
32	02JUL92	.	47.6725	8.91117	30.2070	65.1381	.
33	03JUL92	37.81	43.3168	9.11125	25.4591	61.1745	-5.5068
34	04JUL92	56.01	55.9081	8.99557	38.2771	73.5391	0.1019
35	05JUL92	41.43	61.1407	8.94755	43.6039	78.6776	-19.7107

36	06JUL92	41.42	42.7796	8.92699	25.2831	60.2762	-1.3596
37	07JUL92	64.87	54.6953	8.91806	37.2163	72.1744	10.1747
38	08JUL92	.	73.5462	8.91417	56.0748	91.0177	.
39	09JUL92	48.70	59.9744	9.11350	42.1123	77.8366	-11.2744
40	10JUL92	57.44	56.0101	8.99649	38.3773	73.6428	1.4299
41	11JUL92	49.69	63.0395	8.94794	45.5019	80.5771	-13.3495
42	12JUL92	53.78	64.0271	8.92715	46.5302	81.5240	-10.2471
43	13JUL92	53.47	45.2427	8.91814	27.7635	62.7219	8.2273
44	14JUL92	40.68	50.7310	8.91420	33.2595	68.2025	-10.0510
45	15JUL92	34.75	30.8658	8.91248	13.3977	48.3340	3.8842
46	16JUL92	35.67	41.5735	8.91173	24.1068	59.0402	-5.9035
47	17JUL92	31.15	40.0879	8.91140	22.6219	57.5539	-8.9379
48	18JUL92	39.78	33.1792	8.91125	15.7134	50.6449	6.6008
49	19JUL92	56.23	70.7538	8.91119	53.2882	88.2194	-14.5238
50	20JUL92	74.16
51	21JUL92	49.04	51.3692	9.11125	33.5115	69.2269	-2.3292
52	22JUL92	35.71	30.8028	8.99557	13.1718	48.4338	4.9072
53	23JUL92	31.52	39.4495	8.94755	21.9126	56.9864	-7.9295
54	24JUL92	33.04	38.3068	8.92699	20.8102	55.8034	-5.2668
55	25JUL92	40.65	50.5007	8.91806	33.0217	67.9798	-9.8507
56	26JUL92	38.93	45.7602	8.91417	28.2887	63.2316	-6.8302
57	27JUL92	46.36	36.0857	8.91247	18.6176	53.5538	10.2743
58	28JUL92	48.56	47.5803	8.91172	30.1136	65.0469	0.9797
59	29JUL92	57.61	53.0988	8.91140	35.6328	70.5648	4.5112
60	30JUL92	47.28	43.1727	8.91125	25.7069	60.6384	4.1073
61	31JUL92	37.46	42.0449	8.91119	24.5793	59.5105	-4.5849
62	01AUG92	51.31	52.3051	8.91116	34.8395	69.7706	-0.9951
63	02AUG92	52.54	61.3151	8.91116	43.8495	78.7807	-8.7751
64	03AUG92	60.02	58.2078	8.91116	40.7422	75.6733	1.8122
65	04AUG92	53.06	51.0435	8.91116	33.5779	68.5090	2.0165
66	05AUG92	61.82	58.7871	8.91116	41.3215	76.2527	3.0329
67	06AUG92	85.78	77.6196	8.91116	60.1541	95.0852	8.1604
68	07AUG92	44.76	39.5477	8.91116	22.0822	57.0133	5.2123
69	08AUG92	55.21	42.4226	8.91116	24.9571	59.8882	12.7874
70	09AUG92	49.92	52.9368	8.91116	35.4713	70.4024	-3.0168
71	10AUG92	54.35	56.9933	8.91116	39.5277	74.4588	-2.6433
72	11AUG92	48.51	58.3014	8.91116	40.8358	75.7669	-9.7914
73	12AUG92	48.66	36.0146	8.91116	18.5491	53.4802	12.6454
74	13AUG92	35.30	27.4822	8.91116	10.0167	44.9478	7.8178
75	14AUG92	39.30	42.6036	8.91116	25.1381	60.0692	-3.3036
76	15AUG92	56.81	41.3615	8.91116	23.8960	58.8271	15.4485
77	16AUG92	48.20	41.6379	8.91116	24.1723	59.1034	6.5621
78	17AUG92	39.46	44.8872	8.91116	27.4217	62.3528	-5.4272
79	18AUG92	51.76	48.6345	8.91116	31.1689	66.1000	3.1255
80	19AUG92	69.52	56.4268	8.91116	38.9613	73.8924	13.0932
81	20AUG92	73.20	62.6012	8.91116	45.1357	80.0668	10.5988
82	21AUG92	25.76	42.0489	8.91116	24.5833	59.5145	-16.2889
83	22AUG92	33.71	35.2559	8.91116	17.7904	52.7215	-1.5459
84	23AUG92	34.42	41.4708	8.91116	24.0052	58.9363	-7.0508
85	24AUG92	55.33	50.5741	8.91116	33.1086	68.0397	4.7559
86	25AUG92	62.43	54.0708	8.91116	36.6053	71.5364	8.3592
87	26AUG92	26.35	42.2938	8.91116	24.8283	59.7594	-15.9438
88	27AUG92	23.83	30.6095	8.91116	13.1440	48.0751	-6.7795
89	28AUG92	25.81	35.2953	8.91116	17.8297	52.7608	-9.4853
90	29AUG92	41.32	43.9097	8.91116	26.4442	61.3753	-2.5897
91	30AUG92	57.32	50.4844	8.91116	33.0188	67.9499	6.8356

Appendix B. Application of 1992 model for 1993 Ozone Data

I. Program

```

options
  gunit=pct
  cback=white
  htitle=4
  htext=2
  ftext=swissb
  colors=(black)
  rotate=landscape;

data a;
  infile 'york93.dat';
  input Date mmddyy8. temp relhum pbaro solrad ozone maxo3 CO SO2 NO NOy;
  format Date date.;

proc arima data=a;
  identify var=ozone crosscorr=(relhum pbaro SO2 NOy) noprint;
  estimate p=1 q=1 input=(relhum pbaro SO2 NOy)
    ar=0.87511 ma=0.66201 initval=(-0.75793 relhum
    0.136722 pbaro -0.57661 SO2 1.053324 NOy ) noconstant noest
    method=ml;
  forecast lead=0 id=Date out=folder;

proc print data=folder;
  proc gplot;
    title 'Yorkville 1993';
    plot (forecast ozone)*Date/overlay;
    symbol1 line=2;
    symbol2 line=1;
  end;

proc univariate data=folder;
  var residual;
run;

```

II. Statistical output of 1992 regression model on 1993 ozone data

ARIMA Procedure

Maximum Likelihood Estimation

Parameter	Estimate	Approx.					
		Std Error	T Ratio	Lag	Variable	Shift	
MA1,1	0.66201	0		1	OZONE	0	
AR1,1	0.87511	0		1	OZONE	0	
NUM1	-0.75793	0		0	RELHUM	0	
NUM2	0.13672	0		0	PBARO	0	
NUM3	-0.57661	0		0	SO2	0	
NUM4	1.05332	0		0	NOY	0	

Variance Estimate = 195.664503
 Std Error Estimate = 13.9880128
 AIC = 736.372255
 SBC = 751.371113
 Number of Residuals= 90

Autocorrelation Check of Residuals

Lag	To	Chi	Autocorrelations							
			Square	DF	Prob	0.088	0.095	0.230	0.288	0.154
6	21.41	4	0.000	0.215		0.088	0.095	0.230	0.288	0.154
12	30.80	10	0.001	0.114		0.086	0.156	0.055	0.202	0.047
18	35.23	16	0.004	0.070		0.033	0.115	0.108	-0.086	-0.041
24	39.82	22	0.011	0.063		0.118	-0.025	0.048	0.001	0.130

III. Output of observed and predicted ozone, standard deviation, upper and lower 95% confidence intervals and residuals.

OBS	DATE	OZONE	FORECAST	STD	L95	U95	RESIDUAL
1	01JUN93	55.04
2	02JUN93	68.24
3	03JUN93	71.48	58.6499	15.2842	28.6934	88.6064	12.8301
4	04JUN93	36.20	50.8546	14.4773	22.4796	79.2296	-14.6546
5	05JUN93	44.04	35.6236	14.1902	7.8113	63.4360	8.4164
6	06JUN93	57.28	61.3149	14.0745	33.7294	88.9003	-4.0349
7	07JUN93	62.52	52.7599	14.0255	25.2705	80.2494	9.7601
8	08JUN93	50.84	56.5240	14.0044	29.0759	83.9721	-5.6840
9	09JUN93	42.20	56.4251	13.9952	28.9950	83.8551	-14.2251
10	10JUN93	53.80	55.0555	13.9911	27.6334	82.4777	-1.2555
11	11JUN93	52.28	55.9915	13.9894	28.5728	83.4102	-3.7115
12	12JUN93	84.46	40.9817	13.9886	13.5645	68.3989	43.4783
13	13JUN93	71.88	54.9182	13.9883	27.5017	82.3347	16.9618
14	14JUN93	57.32	46.9154	13.9881	19.4992	74.3316	10.4046
15	15JUN93	65.12	60.6445	13.9880	33.2285	88.0605	4.4755
16	16JUN93	81.56	61.4937	13.9880	34.0777	88.9097	20.0663
17	17JUN93	76.84	70.7463	13.9880	43.3303	98.1623	6.0937
18	18JUN93	77.20	71.1590	13.9880	43.7430	98.575	6.0410
19	19JUN93	73.36	73.1400	13.9880	45.7240	100.556	0.2200
20	20JUN93	58.52	62.1667	13.9880	34.7507	89.583	-3.6467
21	21JUN93	36.36	37.9696	13.9880	10.5536	65.386	-1.6096
22	22JUN93	32.67	46.4388	13.9880	19.0228	73.855	-13.7688
23	23JUN93	93.76	63.6147	13.9880	36.1987	91.031	30.1453
24	24JUN93	65.64	59.2929	13.9880	31.8769	86.709	6.3471
25	25JUN93	41.40	37.8363	13.9880	10.4203	65.252	3.5637
26	26JUN93	44.52	54.0530	13.9880	26.6370	81.469	-9.5330
27	27JUN93	62.28	56.6642	13.9880	29.2482	84.080	5.6158
28	28JUN93	44.16	51.5753	13.9880	24.1593	78.991	-7.4153
29	29JUN93	42.72	41.5124	13.9880	14.0964	68.928	1.2076
30	30JUN93	44.08	49.2412	13.9880	21.8252	76.657	-5.1612
31	01JUL93	46.92	49.2137	13.9880	21.7977	76.630	-2.2937
32	02JUL93	56.76	51.2595	13.9880	23.8435	78.676	5.5005
33	03JUL93	47.28	59.5192	13.9880	32.1032	86.935	-12.2392
34	04JUL93	54.60	59.2284	13.9880	31.8124	86.644	-4.6284
35	05JUL93	40.04	45.9888	13.9880	18.5728	73.4048	-5.9488
36	06JUL93	37.68	58.4776	13.9880	31.0616	85.8936	-20.7976
37	07JUL93	55.20	55.1551	13.9880	27.7391	82.5711	0.0449
38	08JUL93	73.80	50.5884	13.9880	23.1724	78.0044	23.2116
39	09JUL93	69.16	57.7131	13.9880	30.2971	85.1291	11.4469
40	10JUL93	55.52	59.4458	13.9880	32.0298	86.8618	-3.9258
41	11JUL93	41.24	60.3920	13.9880	32.9760	87.8080	-19.1520
42	12JUL93	50.96	51.1649	13.9880	23.7489	78.5809	-0.2049
43	13JUL93	63.00	36.1074	13.9880	8.6913	63.5234	26.8926
44	14JUL93	41.88	55.9865	13.9880	28.5705	83.4025	-14.1065
45	15JUL93	48.56	56.0475	13.9880	28.6315	83.4635	-7.4875
46	16JUL93	45.44	37.0965	13.9880	9.6805	64.5125	8.3435
47	17JUL93	69.08	50.8909	13.9880	23.4749	78.3069	18.1891
48	18JUL93	76.84	61.4443	13.9880	34.0283	88.8603	15.3957
49	19JUL93	52.32	64.2552	13.9880	36.8392	91.6712	-11.9352
50	20JUL93	69.60	60.5386	13.9880	33.1226	87.9546	9.0614
51	21JUL93	88.04	70.2391	13.9880	42.8231	97.6551	17.8009

52	22JUL93	95.12	68.4536	13.9880	41.0376	95.870	26.6664
53	23JUL93	91.60	70.5522	13.9880	43.1362	97.968	21.0478
54	24JUL93	81.40	68.8673	13.9880	41.4513	96.283	12.5327
55	25JUL93	57.20	63.5778	13.9880	36.1618	90.994	-6.3778
56	26JUL93	74.96	65.5030	13.9880	38.0870	92.919	9.4570
57	27JUL93	74.67	69.1706	13.9880	41.7546	96.587	5.4994
58	28JUL93	89.72	71.7687	13.9880	44.3527	99.185	17.9513
59	29JUL93	93.48	74.9488	13.9880	47.5328	102.365	18.5312
60	30JUL93	64.12	84.6861	13.9880	57.2701	112.102	-20.5661
61	31JUL93	71.16	82.6447	13.9880	55.2287	110.061	-11.4847
62	01AUG93	82.04	69.8863	13.9880	42.4703	97.302	12.1537
63	02AUG93	68.44	60.8106	13.9880	33.3946	88.227	7.6294
64	03AUG93	48.87	45.3704	13.9880	17.9544	72.786	3.4996
65	04AUG93	50.40	42.6967	13.9880	15.2807	70.113	7.7033
66	05AUG93	55.88	56.3689	13.9880	28.9529	83.785	-0.4889
67	06AUG93	39.00	34.4386	13.9880	7.0226	61.855	4.5614
68	07AUG93	35.84	35.0836	13.9880	7.6676	62.500	0.7564
69	08AUG93	51.12	49.8953	13.9880	22.4793	77.311	1.2247
70	09AUG93	69.64	54.6847	13.9880	27.2687	82.101	14.9553
71	10AUG93	71.88	63.4367	13.9880	36.0207	90.853	8.4433
72	11AUG93	76.55	77.8721	13.9880	50.4561	105.288	-1.3221
73	12AUG93	64.08	65.5517	13.9880	38.1357	92.968	-1.4717
74	13AUG93	52.08	45.2724	13.9880	17.8564	72.688	6.8076
75	14AUG93	55.24	47.3098	13.9880	19.8938	74.726	7.9302
76	15AUG93	63.16	51.8960	13.9880	24.4800	79.312	11.2640
77	16AUG93	75.00	55.8594	13.9880	28.4434	83.275	19.1406
78	17AUG93	77.52	63.6965	13.9880	36.2805	91.113	13.8235
79	18AUG93	76.24	59.8057	13.9880	32.3897	87.222	16.4343
80	19AUG93	101.64	67.5072	13.9880	40.0912	94.923	34.1328
81	20AUG93	75.96	75.0659	13.9880	47.6499	102.482	0.8941
82	21AUG93	74.12	64.4080	13.9880	36.9920	91.824	9.7120
83	22AUG93	70.60	69.6054	13.9880	42.1894	97.021	0.9946
84	23AUG93	93.84	67.4777	13.9880	40.0617	94.894	26.3623
85	24AUG93	57.42	68.2805	13.9880	40.8645	95.697	-10.8605
86	25AUG93	77.28	61.5506	13.9880	34.1346	88.967	15.7294
87	26AUG93	101.68	75.2405	13.9880	47.8245	102.656	26.4395
88	27AUG93	67.52	76.1929	13.9880	48.7769	103.609	-8.6729
89	28AUG93	73.64	68.8648	13.9880	41.4488	96.281	4.7752
90	29AUG93	70.88	67.8343	13.9880	40.4183	95.250	3.0457
91	30AUG93	60.84	69.7646	13.9880	42.3486	97.181	-8.9246
92	31AUG93	75.96	67.8189	13.9880	40.4029	95.235	8.1411

IV. Descriptive statistics of the residuals

Univariate Procedure

Variable=RESIDUAL

Residual: Actual-Forecast

Moments

N	90	Sum Wgts	90
Mean	4.91295	Sum	442.1655
Std Dev	12.67913	Variance	160.7603
Skewness	0.332227	Kurtosis	0.156777
USS	16480	CSS	14307.67
CV	258.0757	Std Mean	1.336497
T:Mean=0	3.675989	Pr> T	0.0004
Num ^= 0	90	Num > 0	58
M(Sign)	13	Pr>= M	0.0080
Sgn Rank	810.5	Pr>= S	0.0008

Appendix C. Multiple Regression on 1993 ozone data with ARMA errors

I. Program

```

options
  gunit=pct
  cback=white
  htitle=4
  htext=2
  ftext=swissb
  colors=(black)
  rotate=landscape;

data a;
  infile 'york93.dat';
  input Date mmddyy8. temp relhum pbaro solrad ozone maxo3 CO SO2 NO NOy;
  format Date date.;

proc arima;
  identify var=ozone crosscorr=(temp relhum pbaro solrad CO SO2 NOy)
  nointer;
  estimate p=1 q=1 input=(temp relhum CO SO2 NOy)
  noconstant plot method=ml;
  forecast lead=0 id=Date out=folder;

proc arima data=a;
  identify var=ozone crosscorr=(temp relhum pbaro solrad CO SO2 NOy)
  nointer;
  estimate p=1 q=1 input=(temp relhum CO SO2)
  noconstant plot method=ml;
  forecast lead=0 id=Date out=folder2;

proc gplot data=folder;
  title 'Yorkville 1993';
  plot (forecast ozone)*Date/overlay;
  symbol1 line=2;
  symbol2 line=1;

proc print data=folder;
run;

```

II. Statistical output of 1993 regression (NOy is included in regression)

ARIMA Procedure

Maximum Likelihood Estimation

Parameter	Estimate	Std Error	Approx.			
			T Ratio	Lag	Variable	Shift
MA1,1	0.54244	0.11502	4.72	1	OZONE	0
AR1,1	0.94866	0.04309	22.01	1	OZONE	0
NUM1	1.62859	0.21083	7.72	0	TEMP	0
NUM2	-0.53881	0.07426	-7.26	0	RELHUM	0
NUM3	0.15885	0.02271	7.00	0	CO	0
NUM4	0.28976	0.14814	1.96	0	SO2	0
NUM5	1.02496	0.59466	1.72	0	NOY	0

Variance Estimate = 51.0245468
 Std Error Estimate = 7.14314684
 AIC = 617.234365
 SBC = 634.733033
 Number of Residuals= 90

Correlations of the Estimates

Variable	Parameter	OZONE MA1,1	OZONE AR1,1	TEMP NUM1	RELHUM NUM2	CO NUM3
OZONE	MA1,1	1.000	0.582	0.012	0.080	-0.043
OZONE	AR1,1	0.582	1.000	0.020	-0.107	0.142
TEMP	NUM1	0.012	0.020	1.000	-0.057	-0.264
RELHUM	NUM2	0.080	-0.107	-0.057	1.000	-0.643
CO	NUM3	-0.043	0.142	-0.264	-0.643	1.000
SO2	NUM4	-0.087	0.090	-0.102	-0.267	0.479
NOY	NUM5	0.092	-0.120	-0.014	0.520	-0.761
Variable	Parameter		SO2 NUM4		NOY NUM5	
OZONE	MA1,1		-0.087		0.092	
OZONE	AR1,1		0.090		-0.120	
TEMP	NUM1		-0.102		-0.014	
RELHUM	NUM2		-0.267		0.520	
CO	NUM3		0.479		-0.761	
SO2	NUM4		1.000		-0.653	
NOY	NUM5		-0.653		1.000	

Autocorrelation Check of Residuals

To	Chi	Autocorrelations							
Lag	Square DF	Prob							
6	2.50	4	0.645	-0.012	-0.006	0.103	0.016	0.121	0.008
12	8.62	10	0.568	-0.034	0.002	-0.225	-0.063	0.058	0.025
18	16.28	16	0.434	0.043	-0.170	-0.010	0.183	0.033	0.060
24	20.43	22	0.556	0.097	0.098	0.012	-0.091	0.078	0.032

Model for variable OZONE

No mean term in this model.

Autoregressive Factors
Factor 1: 1 - 0.94866 B**(1)

Moving Average Factors
Factor 1: 1 - 0.54244 B**(1)

Input Number 1 is TEMP.
Overall Regression Factor = 1.628593

Input Number 2 is RELHUM.
Overall Regression Factor = -0.53881

Input Number 3 is CO.
Overall Regression Factor = 0.158854

Input Number 4 is SO2.
Overall Regression Factor = 0.289762

Input Number 5 is NOY.
Overall Regression Factor = 1.024958

III. Statistical output of multiple regression on the 1993 ozone data with NOy removed

ARIMA Procedure

Maximum Likelihood Estimation

Parameter	Estimate	Std Error	T Ratio	Lag	Variable	Shift
MA1,1	0.53400	0.11144	4.79	1	OZONE	0
AR1,1	0.95798	0.03840	24.95	1	OZONE	0
NUM1	1.61859	0.23266	6.96	0	TEMP	0
NUM2	-0.60666	0.06564	-9.24	0	RELHUM	0
NUM3	0.18906	0.01480	12.78	0	CO	0
NUM4	0.45282	0.11242	4.03	0	SO2	0

Variance Estimate = 52.0935906
 Std Error Estimate = 7.21758897
 AIC = 618.373558
 SBC = 633.372416
 Number of Residuals= 90

Autocorrelation Check of Residuals

To	Chi	Autocorrelations							
Lag	Square	DF	Prob						
6	3.63	4	0.458	-0.017	-0.008	0.143	-0.001	0.130	0.001
12	10.32	10	0.413	-0.024	0.034	-0.243	-0.038	0.043	-0.038
18	19.68	16	0.235	0.067	-0.176	-0.028	0.204	-0.006	0.082
24	23.52	22	0.373	0.054	0.123	0.062	-0.075	0.052	0.043

Model for variable OZONE

No mean term in this model.

Autoregressive Factors
 Factor 1: 1 - 0.95798 B**(1)

Moving Average Factors
 Factor 1: 1 - 0.534 B**(1)

Input Number 1 is TEMP.
 Overall Regression Factor = 1.618591

Input Number 2 is RELHUM.
 Overall Regression Factor = -0.60666

Input Number 3 is CO.
 Overall Regression Factor = 0.189061

Input Number 4 is SO2.
 Overall Regression Factor = 0.452822

IV. Observed and predicted ozone, standard deviation, 95% confidence intervals and residuals (from 1993 regression that includes the NO_y variable)

OBS	DATE	OZONE	FORECAST	STD	L95	U95	RESIDUAL
1	01JUN93	55.04
2	02JUN93	68.24
3	03JUN93	71.48	65.8940	11.6266	43.1063	88.6817	5.5860
4	04JUN93	36.20	55.6115	7.7699	40.3828	70.8402	-19.4115
5	05JUN93	44.04	41.2274	7.3040	26.9118	55.5430	2.8126
6	06JUN93	57.28	53.9778	7.1888	39.8880	68.0676	3.3022
7	07JUN93	62.52	70.5505	7.1564	56.5242	84.5769	-8.0305
8	08JUN93	50.84	56.6778	7.1470	42.6699	70.6858	-5.8378
9	09JUN93	42.20	49.0256	7.1443	35.0230	63.0282	-6.8256
10	10JUN93	53.80	52.0610	7.1435	38.0600	66.0620	1.7390
11	11JUN93	52.28	54.5785	7.1432	40.5780	68.5791	-2.2985
12	12JUN93	84.46	76.1472	7.1431	62.1469	90.1475	8.3128
13	13JUN93	71.88	63.9261	7.1431	49.9258	77.9264	7.9539
14	14JUN93	57.32	71.9026	7.1431	57.9022	85.9029	-14.5826
15	15JUN93	65.12	56.9703	7.1431	42.9700	70.9706	8.1497
16	16JUN93	81.56	73.7138	7.1431	59.7135	87.7141	7.8462
17	17JUN93	76.84	74.6258	7.1431	60.6255	88.6261	2.2142
18	18JUN93	77.20	73.4532	7.14315	59.4529	87.454	3.7468
19	19JUN93	73.36	69.2852	7.14315	55.2849	83.285	4.0748
20	20JUN93	58.52	70.6697	7.14315	56.6694	84.670	-12.1497
21	21JUN93	36.36	34.2456	7.14315	20.2453	48.246	2.1144
22	22JUN93	32.67	40.8658	7.14315	26.8655	54.866	-8.1958
23	23JUN93	93.76	86.4889	7.14315	72.4886	100.489	7.2711
24	24JUN93	65.64	72.3113	7.14315	58.3109	86.312	-6.6713
25	25JUN93	41.40	53.5279	7.14315	39.5276	67.528	-12.1279
26	26JUN93	44.52	43.6802	7.14315	29.6799	57.681	0.8398
27	27JUN93	62.28	60.3573	7.14315	46.3570	74.358	1.9227
28	28JUN93	44.16	43.3208	7.14315	29.3205	57.321	0.8392
29	29JUN93	42.72	43.6092	7.14315	29.6088	57.609	-0.8892
30	30JUN93	44.08	51.2911	7.14315	37.2908	65.291	-7.2111
31	01JUL93	46.92	48.9135	7.14315	34.9132	62.914	-1.9935
32	02JUL93	56.76	52.4943	7.14315	38.4940	66.495	4.2657
33	03JUL93	47.28	54.0724	7.14315	40.0721	68.073	-6.7924
34	04JUL93	54.60	60.7313	7.14315	46.7309	74.732	-6.1313
35	05JUL93	40.04	39.4462	7.14315	25.4459	53.4465	0.5938
36	06JUL93	37.68	51.8667	7.14315	37.8664	65.8670	-14.1867
37	07JUL93	55.20	58.7050	7.14315	44.7047	72.7053	-3.5050
38	08JUL93	73.80	73.9004	7.14315	59.9001	87.9008	-0.1004
39	09JUL93	69.16	61.3399	7.14315	47.3396	75.3402	7.8201
40	10JUL93	55.52	58.8754	7.14315	44.8751	72.8758	-3.3554
41	11JUL93	41.24	44.3816	7.14315	30.3813	58.3819	-3.1416
42	12JUL93	50.96	47.4887	7.14315	33.4884	61.4890	3.4713
43	13JUL93	63.00	61.0294	7.14315	47.0291	75.0297	1.9706
44	14JUL93	41.88	43.8170	7.14315	29.8167	57.8173	-1.9370
45	15JUL93	48.56	48.4649	7.14315	34.4646	62.4652	0.0951
46	16JUL93	45.44	43.1486	7.14315	29.1483	57.1489	2.2914
47	17JUL93	69.08	63.2411	7.14315	49.2408	77.2414	5.8389
48	18JUL93	76.84	74.5920	7.14315	60.5916	88.5923	2.2480
49	19JUL93	52.32	66.6568	7.14315	52.6565	80.6571	-14.3368
50	20JUL93	69.60	58.8327	7.14315	44.8324	72.8330	10.7673
51	21JUL93	88.04	80.9423	7.14315	66.9420	94.9426	7.0977
52	22JUL93	95.12	91.9776	7.14315	77.9773	105.978	3.1424
53	23JUL93	91.60	94.9329	7.14315	80.9326	108.933	-3.3329
54	24JUL93	81.40	80.9557	7.14315	66.9554	94.956	0.4443
55	25JUL93	57.20	65.1737	7.14315	51.1734	79.174	-7.9737
56	26JUL93	74.96	77.9551	7.14315	63.9548	91.955	-2.9951
57	27JUL93	74.67	75.2995	7.14315	61.2992	89.300	-0.6295
58	28JUL93	89.72	80.4016	7.14315	66.4013	94.402	9.3184
59	29JUL93	93.48	79.8823	7.14315	65.8820	93.883	13.5977
60	30JUL93	64.12	64.5478	7.14315	50.5475	78.548	-0.4278

61	31JUL93	71.16	71.4109	7.14315	57.4106	85.411	-0.2509
62	01AUG93	82.04	69.5280	7.14315	55.5277	83.528	12.5120
63	02AUG93	68.44	68.1764	7.14315	54.1761	82.177	0.2636
64	03AUG93	48.87	39.3754	7.14315	25.3751	53.376	9.4946
65	04AUG93	50.40	47.8113	7.14315	33.8110	61.812	2.5887
66	05AUG93	55.88	58.3703	7.14315	44.3700	72.371	-2.4903
67	06AUG93	39.00	31.7075	7.14315	17.7072	45.708	7.2925
68	07AUG93	35.84	43.1916	7.14315	29.1913	57.192	-7.3516
69	08AUG93	51.12	48.4239	7.14315	34.4236	62.424	2.6961
70	09AUG93	69.64	68.7672	7.14315	54.7669	82.767	0.8728
71	10AUG93	71.88	71.0996	7.14315	57.0993	85.100	0.7804
72	11AUG93	76.55	89.6603	7.14315	75.6599	103.661	-13.1103
73	12AUG93	64.08	72.6781	7.14315	58.6777	86.678	-8.5981
74	13AUG93	52.08	52.7281	7.14315	38.7277	66.728	-0.6481
75	14AUG93	55.24	49.7652	7.14315	35.7649	63.766	5.4748
76	15AUG93	63.16	63.1766	7.14315	49.1763	77.177	-0.0166
77	16AUG93	75.00	69.7847	7.14315	55.7844	83.785	5.2153
78	17AUG93	77.52	75.1357	7.14315	61.1354	89.136	2.3843
79	18AUG93	76.24	65.5987	7.14315	51.5984	79.599	10.6413
80	19AUG93	101.64	90.7582	7.14315	76.7579	104.759	10.8818
81	20AUG93	75.96	76.8325	7.14315	62.8322	90.833	-0.8725
82	21AUG93	74.12	60.1109	7.14315	46.1106	74.111	14.0091
83	22AUG93	70.60	68.3250	7.14315	54.3247	82.325	2.2750
84	23AUG93	93.84	98.5485	7.14315	84.5482	112.549	-4.7085
85	24AUG93	57.42	53.9654	7.14315	39.9650	67.966	3.4546
86	25AUG93	77.28	76.8137	7.14315	62.8134	90.814	0.4663
87	26AUG93	101.68	94.4690	7.14315	80.4686	108.469	7.2110
88	27AUG93	67.52	62.5746	7.14315	48.5743	76.575	4.9454
89	28AUG93	73.64	74.3456	7.14315	60.3453	88.346	-0.7056
90	29AUG93	70.88	70.7708	7.14315	56.7705	84.771	0.1092
91	30AUG93	60.84	76.0581	7.14315	62.0578	90.058	-15.2181
92	31AUG93	75.96	69.8248	7.14315	55.8245	83.825	6.1352

Appendix D. Yorkville 1992 and 1993 Data

I. Yorkville 1992 meteorological and gas data

Date	TEMP	RELHUM	pBARO	SOLRAD	OZONE	maxO3	CO	SO2	NO	NOy
6-1-92	15.30	74.80	728.14	408.52	46.46	58	262.40	14.14	2.72	16.98
6-2-92	21.56	58.18	727.31	621.08	81.46	94	276.16	2.76	0.43	14.49
6-3-92	16.74	98.08	724.26	129.84	35.76	39	242.44	5.78	0.58	5.71
6-4-92	20.91	73.02	720.38	434.04	57.04	64	194.20	1.78	0.24	6.42
6-5-92	22.68	69.72	722.61	664.72	55.34	65	206.33	1.62	0.61	9.08
6-6-92	26.29	56.03	726.03	785.52	65.40	68	241.00	2.34	0.30	11.57
6-7-92	26.60	72.08	728.58	668.64	49.70	56	239.00	0.78	0.27	7.08
6-8-92	19.60	93.10	728.58	376.20	18.81	25	211.36	19.99	3.42	10.45
6-9-92	20.62	91.25	725.26	501.12	24.18	37	.	0.56	0.36	1.86
6-10-92	25.90	77.41	725.97	630.84	48.88	59	122.63	2.18	0.37	8.59
6-11-92	24.20	88.08	726.41	356.64	57.26	72	281.08	4.04	0.96	13.35
6-12-92	16.56	93.03	728.02	150.96	44.92	48	293.72	0.19	1.32	15.47
6-13-92	18.30	99.10	726.08	138.88	24.78	33	304.00	0.46	2.45	15.00
6-14-92	23.63	85.80	725.46	472.04	40.47	48	181.16	0.26	0.21	8.47
6-15-92	26.90	73.78	726.97	547.38	52.13	58	213.63	0.57	0.27	6.04
6-16-92	28.49	66.84	729.59	591.92	81.83	101	224.88	6.24	0.33	13.92
6-17-92	26.16	78.13	731.48	591.44	56.92	63	233.40	0.41	0.83	12.46
6-18-92	26.58	78.80	729.53	471.00	41.67	53	210.00	23.26	3.10	17.45
6-19-92	27.68	65.77	725.23	801.64	65.62	77	223.68	4.17	0.40	11.96
6-20-92	26.51	56.34	723.95	792.96	67.74	74	203.40	3.07	0.32	7.09
6-21-92	23.25	73.94	725.81	649.84	52.41	64	221.48	1.31	0.34	5.55
6-22-92	25.08	60.75	727.25	687.00	68.88	89	193.50	6.11	2.20	19.33
6-23-92	25.57	55.41	725.66	788.60	81.63	107	229.60	8.35	0.39	12.02
6-24-92	22.97	48.76	723.77	826.48	64.81	71	221.36	1.23	0.26	8.02
6-25-92	23.49	58.78	724.32	727.68	64.44	70	231.56	2.40	0.34	8.19
6-26-92	22.18	75.01	724.31	600.24	58.90	67	245.24	2.77	0.40	7.99
6-27-92	20.84	74.64	724.60	638.08	57.88	72	257.88	2.22	0.50	8.10
6-28-92	19.97	75.82	725.03	552.36	75.90	87	234.20	5.67	0.69	14.11
6-29-92	26.70	61.76	726.10	694.60	76.08	83	178.44	10.13	0.46	14.23
6-30-92	23.55	81.65	725.46	463.04	46.46	55	126.04	12.49	0.99	7.88
7-1-92	24.12	89.38	726.23	504.38	33.26	48	162.21	0.66	0.42	3.02
7-2-92	26.27	80.74	727.55	603.32	.	.	175.56	0.24	0.39	4.86
7-3-92	24.00	86.80	729.34	.	37.81	44	204.56	0.21	0.91	5.36
7-4-92	27.65	68.60	731.11	.	56.01	66	187.44	2.20	0.30	6.80
7-5-92	29.09	62.20	728.03	.	41.43	50	146.44	0.44	0.23	6.82
7-6-92	27.43	77.48	727.36	.	41.42	47	166.52	1.20	0.69	5.19
7-7-92	30.38	66.93	730.60	.	64.87	83	181.84	8.55	0.90	12.47
7-8-92	31.86	47.74	732.03	.	.	.	167.92	1.01	1.67	9.86
7-9-92	30.83	61.07	731.44	.	48.70	55	189.28	1.33	0.38	6.80
7-10-92	31.20	64.24	731.12	.	57.44	64	222.40	2.71	0.46	8.69
7-11-92	31.28	57.62	730.83	.	49.69	59	160.16	1.48	1.03	9.32
7-12-92	33.03	50.28	730.74	.	53.78	67	194.56	4.44	0.60	9.12
7-13-92	30.06	72.13	730.66	.	53.47	61	227.52	4.14	0.39	8.38
7-14-92	29.39	65.76	729.68	.	40.68	50	184.00	2.46	0.37	5.78

7-15-92	24.86	88.26	728.10	.	34.75	45	248.32	2.76	0.74	5.06
7-16-92	27.28	76.97	729.67	.	35.67	40	217.12	0.94	0.35	4.46
7-17-92	27.35	77.54	731.04	.	31.15	39	223.72	2.38	0.56	4.79
7-18-92	24.22	83.84	731.72	.	39.78	50	229.64	1.65	0.42	3.52
7-19-92	.	64.78	731.38	.	56.23	72	268.48	27.36	10.04	37.54
7-20-92	.	60.31	.	.	74.16	81	301.24	3.78	0.27	13.76
7-21-92	25.96	66.75	730.50	.	49.04	54	211.54	3.30	0.33	9.20
7-22-92	23.46	90.78	730.38	.	35.71	41	205.09	0.45	1.17	5.28
7-23-92	26.22	80.08	731.90	.	31.52	37	170.72	1.01	0.45	4.19
7-24-92	26.97	80.40	733.37	.	33.04	41	161.28	2.08	0.49	4.93
7-25-92	22.28	67.26	732.71	.	40.65	50	151.68	2.72	0.65	7.97
7-26-92	26.57	71.92	729.36	.	38.93	50	166.84	3.04	0.72	8.78
7-27-92	25.02	81.18	727.30	.	46.36	54	182.16	0.78	0.39	5.85
7-28-92	24.80	72.08	728.75	542.92	48.56	62	208.72	0.94	0.55	7.14
7-29-92	27.27	67.07	728.72	655.56	57.61	67	189.24	1.20	0.38	8.20
7-30-92	26.05	80.49	729.14	613.96	47.28	54	160.44	1.76	0.51	7.34
7-31-92	26.09	79.96	729.03	507.84	37.46	43	130.44	1.40	0.40	4.61
8-1-92	23.82	69.86	731.04	727.80	51.31	57	171.76	1.98	0.44	7.94
8-2-92	25.05	57.91	730.36	772.20	52.54	55	153.76	0.98	0.30	7.41
8-3-92	22.28	56.95	728.65	755.48	60.02	68	165.16	7.15	0.64	8.92
8-4-92	22.40	69.94	728.38	617.36	53.06	57	176.72	0.80	0.31	7.24
8-5-92	26.10	62.88	730.31	748.48	61.82	73	195.72	2.42	0.35	9.42
8-6-92	24.10	80.56	731.25	382.64	85.78	113	344.17	8.40	4.71	42.33
8-7-92	23.23	90.05	731.96	376.92	44.76	60	227.32	0.97	0.61	7.08
8-8-92	26.52	76.74	732.60	442.80	55.21	59	152.92	16.00	0.30	7.42
8-9-92	27.80	71.90	731.71	619.48	49.92	57	144.24	4.61	0.17	5.43
8-10-92	29.11	67.52	729.12	748.91	54.35	60	201.43	2.20	0.19	6.27
8-11-92	27.67	62.06	728.56	752.48	48.51	59	274.92	3.18	0.22	5.10
8-12-92	25.73	83.02	729.32	321.60	48.66	69	.	11.50	0.25	5.72
8-13-92	18.68	99.97	728.44	100.80	35.30	40	160.08	4.08	0.22	3.29
8-14-92	23.54	72.92	729.36	657.92	39.30	59	134.23	35.24	4.50	13.84
8-15-92	22.52	78.65	729.25	346.33	56.81	72	178.24	15.77	0.39	7.27
8-16-92	21.35	90.54	729.62	318.56	48.20	62	291.84	1.64	0.32	5.50
8-17-92	.	86.49	729.94	442.72	39.46	55	211.12	1.38	0.47	4.83
8-18-92	.	77.69	731.13	565.60	51.76	66	204.92	3.24	0.28	4.77
8-19-92	24.39	65.05	729.62	476.04	69.52	74	222.00	9.82	0.18	6.76
8-20-92	24.55	63.26	728.85	560.92	73.20	91	267.20	9.18	0.18	8.97
8-21-92	.	100.00	731.18	83.60	25.76	39	353.12	4.38	1.21	11.62
8-22-92	23.48	88.75	731.94	288.00	33.71	42	206.80	14.50	0.52	6.78
8-23-92	24.34	86.04	733.37	477.08	34.42	41	211.88	4.96	0.45	6.07
8-24-92	25.18	77.07	734.79	577.60	55.33	66	155.16	2.18	0.68	8.32
8-25-92	21.30	71.89	734.08	530.32	62.43	76	170.84	6.12	0.75	9.32
8-26-92	26.59	81.26	732.20	463.48	26.35	36	189.35	9.70	0.58	5.62
8-27-92	23.10	90.58	725.81	301.64	23.83	27	160.28	6.80	0.76	4.11
8-28-92	20.02	85.44	727.03	444.40	25.81	41	164.57	2.62	0.65	3.74
8-29-92	20.60	68.97	730.14	759.36	41.32	55	139.00	22.09	3.65	12.03
8-30-92	23.78	64.68	731.82	634.16	57.32	73	135.44	3.39	0.14	4.83
8-31-92	24.51	64.29	732.08	674.20	76.30	86	131.72	.	0.31	10.84

II. Yorkville 1993 meteorological and gas data

York	TEMP	RELHUM	pBARO	SOLRAD	OZONE	maxO3	CO	SO2	NO	NOy
6-1-93	.	.	.	902.13	55.04	63	293.16	2.08	0.38	4.07
6-2-93	.	.	.	794.88	68.24	83	374.60	4.96	0.60	6.99
6-3-93	26.59	56.94	723.66	869.68	71.48	83	300.96	3.14	0.17	4.44
6-4-93	26.54	72.32	723.67	786.00	36.20	39	277.80	0.62	0.27	2.82
6-5-93	24.85	87.38	726.75	397.38	44.04	50	315.67	0.80	0.24	2.96
6-6-93	23.34	56.66	730.05	877.32	57.28	73	289.44	2.38	0.22	3.81
6-7-93	28.64	64.48	729.54	793.72	62.52	72	344.84	6.12	0.26	4.49
6-8-93	29.27	63.20	727.98	806.48	50.84	57	280.20	2.45	0.29	3.41
6-9-93	29.00	61.16	728.86	828.88	42.20	54	246.12	1.73	0.25	2.82
6-10-93	28.63	58.81	729.78	790.00	53.80	61	271.32	2.71	0.23	3.27
6-11-93	28.72	58.33	729.63	844.44	52.28	55	280.68	1.31	0.22	3.08
6-12-93	27.69	64.90	729.14	746.16	84.46	119	344.60	32.20	0.72	11.04
6-13-93	25.91	72.63	729.07	707.04	71.88	75	373.00	4.62	0.24	5.64
6-14-93	21.48	91.27	729.12	371.16	57.32	74	502.32	2.14	0.73	7.49
6-15-93	25.39	71.23	729.31	583.50	65.12	70	355.56	1.50	0.24	4.78
6-16-93	27.44	64.90	730.18	738.88	81.56	97	351.28	13.89	0.34	8.07
6-17-93	27.38	59.50	732.74	840.12	76.84	110	337.80	8.09	0.48	6.63
6-18-93	27.22	63.35	733.10	753.40	77.20	100	346.76	2.51	0.50	7.04
6-19-93	26.41	59.20	731.54	749.68	73.36	92	305.44	3.18	0.25	6.82
6-20-93	26.79	56.45	730.73	590.76	58.52	70	255.16	22.94	0.50	6.80
6-21-93	20.04	97.39	729.50	284.00	36.36	42	315.12	3.30	0.47	4.75
6-22-93	23.70	82.71	726.77	429.43	32.67	42	280.16	1.13	0.27	2.78
6-23-93	27.82	61.50	727.56	811.44	93.76	104	423.20	5.03	0.32	9.53
6-24-93	26.24	74.95	730.07	560.64	65.64	80	398.80	1.25	0.41	7.04
6-25-93	23.11	87.56	731.17	.	41.40	57	327.00	23.64	1.29	7.71
6-26-93	25.69	76.17	729.15	.	44.52	56	300.40	0.94	0.27	3.18
6-27-93	27.35	67.64	727.10	.	62.28	69	331.16	5.75	0.21	5.45
6-28-93	25.53	75.58	727.08	.	44.16	48	284.64	0.98	0.23	3.31
6-29-93	24.55	84.53	726.96	.	42.72	45	321.36	2.21	0.29	3.16
6-30-93	27.79	75.16	727.57	.	44.08	48	305.52	1.22	0.27	3.38
7-1-93	28.80	72.41	727.98	.	46.92	52	286.56	2.05	0.26	3.28
7-2-93	28.88	67.98	728.54	.	56.76	70	285.56	4.63	0.26	4.11
7-3-93	29.73	59.90	727.96	829.68	47.28	50	257.24	1.05	0.20	3.32
7-4-93	31.04	56.04	729.37	796.00	54.60	59	272.32	4.51	0.24	4.75
7-5-93	28.15	70.86	729.32	654.40	40.04	47	253.04	1.61	0.21	2.15
7-6-93	30.20	54.70	730.24	845.28	37.68	43	243.08	1.57	0.22	3.28
7-7-93	31.26	52.14	729.64	799.92	55.20	69	281.52	6.14	0.25	4.78
7-8-93	31.46	56.86	729.03	818.44	73.80	100	351.04	16.35	0.69	8.72
7-9-93	30.02	57.45	729.95	835.96	69.16	79	324.44	6.72	0.21	5.14
7-10-93	30.06	60.56	730.70	741.64	55.52	60	311.20	1.77	0.20	3.89
7-11-93	29.58	55.10	729.34	831.56	41.24	49	217.76	2.70	0.23	2.62
7-12-93	28.93	60.75	726.22	776.46	50.96	72	260.68	4.25	0.23	3.20
7-13-93	28.03	72.00	728.35	660.83	63.00	69	312.16	25.15	0.46	7.85
7-14-93	27.88	68.34	730.68	675.87	41.88	45	248.57	0.91	1.77	4.76
7-15-93	29.43	60.81	729.70	753.60	48.56	58	247.48	1.58	0.18	3.15
7-16-93	26.17	83.90	728.28	346.00	45.44	51	319.52	1.73	0.32	3.55
7-17-93	29.06	67.96	727.97	550.56	69.08	86	338.00	4.88	0.21	5.06
7-18-93	31.09	60.89	729.06	663.36	76.84	87	336.68	5.46	0.25	6.53

7-19-93	31.69	60.60	728.17	645.40	52.32	66	294.20	1.41	0.25	4.27
7-20-93	30.81	59.52	727.97	842.28	69.60	76	283.24	3.13	0.22	4.17
7-21-93	31.40	51.69	727.51	840.88	88.04	123	334.24	5.12	0.21	7.48
7-22-93	32.39	55.33	727.15	750.17	95.12	114	383.60	8.07	0.16	7.06
7-23-93	31.16	60.78	727.00	690.92	91.60	105	416.12	7.87	0.27	8.46
7-24-93	30.88	63.41	728.59	684.04	81.40	114	365.12	7.94	0.23	5.85
7-25-93	29.79	73.21	729.43	577.36	57.20	69	319.20	4.45	0.31	5.19
7-26-93	31.51	64.96	728.28	696.60	74.96	103	348.16	10.15	0.30	7.59
7-27-93	31.14	61.67	727.55	662.92	74.67	85	343.00	6.77	0.38	6.58
7-28-93	32.18	56.70	728.34	766.32	89.72	104	325.16	11.82	0.35	8.61
7-29-93	32.70	57.39	727.85	759.08	93.48	117	308.44	7.22	0.27	7.57
7-30-93	28.81	44.45	727.18	863.80	64.12	72	201.48	4.18	0.20	3.97
7-31-93	29.18	35.28	728.00	878.68	71.16	76	180.64	13.03	0.59	6.37
8-1-93	30.22	47.09	727.30	642.36	82.04	94	225.44	8.22	0.09	3.80
8-2-93	29.46	64.29	726.71	659.92	68.44	78	266.68	2.88	0.16	3.07
8-3-93	23.11	86.12	730.67	362.48	48.87	54	235.83	1.14	0.14	2.13
8-4-93	24.02	88.64	732.24	417.40	50.40	61	269.96	1.16	0.11	1.59
8-5-93	26.28	72.68	730.69	627.36	55.88	61	243.84	2.06	0.18	3.26
8-6-93	21.48	98.19	728.36	214.68	39.00	45	237.88	0.25	0.03	1.31
8-7-93	22.08	98.03	729.62	267.20	35.84	41	280.12	1.32	0.30	2.26
8-8-93	25.10	78.64	732.58	719.21	51.12	60	233.88	1.70	0.17	2.99
8-9-93	26.65	69.05	732.71	697.96	69.64	76	286.20	8.20	0.28	4.78
8-10-93	26.56	66.83	731.67	700.80	71.88	82	301.24	1.54	0.61	5.73
8-11-93	27.26	60.84	731.07	688.04	76.55	92	337.65	1.01	0.23	14.26
8-12-93	28.15	60.26	730.06	698.32	64.08	76	310.04	3.71	0.07	5.16
8-13-93	26.02	85.74	728.06	314.16	52.08	63	314.96	3.16	0.19	5.46
8-14-93	26.31	83.05	727.56	508.80	55.24	60	296.60	1.77	0.09	4.19
8-15-93	27.32	79.67	728.49	562.04	63.16	72	341.36	1.18	0.13	4.94
8-16-93	29.57	66.00	729.42	646.88	75.00	86	281.76	16.28	0.12	5.70
8-17-93	30.42	68.24	728.55	706.28	77.52	85	322.12	4.71	0.09	5.79
8-18-93	29.15	72.93	727.17	521.00	76.24	89	276.60	8.26	0.14	6.27
8-19-93	29.08	74.10	728.56	660.96	101.64	115	401.84	2.95	0.17	9.65
8-20-93	30.46	64.78	728.34	703.92	75.96	82	268.54	3.75	0.08	5.53
8-21-93	28.27	74.84	728.14	642.88	74.12	100	219.16	5.73	0.11	6.06
8-22-93	28.83	66.11	728.65	1.16	70.60	83	207.16	6.47	0.11	5.28
8-23-93	28.40	75.31	728.98	1.44	93.84	118	387.84	6.98	0.43	12.08
8-24-93	28.19	71.26	729.76	2.00	57.42	63	172.58	2.70	0.25	4.07
8-25-93	28.59	66.27	731.76	2.04	77.28	107	214.20	23.92	0.59	9.99
8-26-93	28.86	65.11	731.87	2.40	101.68	133	356.16	4.64	0.14	10.18
8-27-93	28.67	62.32	730.26	2.91	67.52	84	162.87	4.42	0.22	5.77
8-28-93	29.24	67.17	728.76	3.00	73.64	91	234.68	4.42	0.14	6.63
8-29-93	28.77	66.22	728.21	3.00	70.88	90	225.20	4.52	0.24	5.99
8-30-93	28.65	64.56	728.34	3.00	60.84	88	241.56	5.68	1.01	8.38
8-31-93	29.39	61.66	727.64	267.40	75.96	117	248.65	2.50	0.14	6.21

References

Brocklebank, John C., David A. Dickey. *SAS® System for Forecasting Time Series*. Cary, NC: SAS Institute Inc., 1986.

Chameides, W.L., R.W. Lindsay, J. Richardson, C.S. Kiang. The Role of Biogenic Hydrocarbons in Urban Photochemical Smog: Atlanta as a Case Study. *Science 241*, 1473-1474, 1988.

Chock, David P., Sudarshan Kumar and Richard Herrmann. An analysis of trends in oxidant air quality in the south cast air basin of California. *Atmospheric Environment 16*, 2615-2624, 1982.

Hurley, P.J., and P.C. Manins. Meteorological modeling on high-ozone days in Perth, Western Australia. *Journal of Applied Meteorology 34*, 1995.

Kirk, David. Environmental Science and Engineering, Gainesville, FL, personal communication, March 6, 1996.

Korsog, Patricia E., and George T. Wolff. An examination of urban ozone trends in the northeastern U.S. (1973-1983) using a robust statistical method. *Atmospheric Environment 25B*, 47-57, 1991.

Kumar, Sudarshan, and David P. Chock. An update on oxidant trends in the south coast air basin of California. *Atmospheric Environment 18*, 2131-2134, 1984.

Niccum, Elizabeth M., Donald E. Lehrman and William R. Knuth. The influence of meteorology on the air quality in the San Luis Obispo County-Southwestern San Joquin Valley region for 3-6 August 1990. *Journal of Applied Meteorology 34*, 1834-1847, 1995.

SAS/ETS® User's Guide, Version 6, First Edition. Cary, NC: SAS Institute Inc., 1988.

Speckman, Paul. *Statistics 518: Applied Time Series Analysis*. Raleigh: North Carolina State University, graduate level statistics course, fall semester 1995.

The State of the Southern Oxidants Study (SOS): Policy-Relevant Findings in Ozone Pollution Research 1988 - 1994. Ed. W.L. Chameides and Ellis B. Cowling. Raleigh NC: Southern Oxidants Study, 1995.

Trainer, M., E.Y. Hsie, S.A. McKeen, R. Tallamraju, D.D. Parrish, F.C. Fehsenfeld, and S.C. Liu. Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site. *J. Geophys. Res. 92*, 11879-11894, 1987.

Trainer, M., E.J. Williams, D.D. Parrish, M.P. Buhr, E.J. Allwine, H.H. Westberg, F.C. Fehsenfeld, and S.C. Liu. Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature* 329, 705-707, 1987.

U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center. United States seasonal climate summary, summer (June-August) 1992. *Weekly Climate Bulletin*. Ed. Richard Tinker. No. 92/37. Washington DC: Govt. Printing Office, September 12, 1992.

U.S. Dept. of Commerce. NOAA. National Weather Service. Climate Analysis Center. *Weekly Climate Bulletin*. Ed. Richard Tinker. No. 93/39. Washington DC: Govt. Printing Office, September 29, 1993.

Vukovich, Fred M. Boundary layer ozone variations in the eastern United States and their association with meteorological variations: long-term variations. *J. Geophys. Res.* 99, 16839-16850, 1994.

Vukovich, Fred M., Walter D. Bach, Jr., Bobby W. Crissman and William J. King. On the relationship between high ozone in the rural surface layer and high pressure systems. *Atmospheric Environment* 11, 967-983, 1977.

Wei, William W. S. *Time Series Analysis: Univariate and Multivariate Methods*. Redwood City CA: Addison-Wesley Publishing Company, Inc., 1990.